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Extraction of Pesticides from Process Streams Using High Volatility Solvents A Feasibility Study

S-Cubed, La Jolla, CA

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Extraction of Pesticides from Process Streams Using High Volatility Solvents

A Feasibility Study

by

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The report gives results of a program to determine the feasibility of extracting pesticides from process streams using a liquid-liquid solvent extraction approach. A brief literature review provided foundational data in support of the technology identified for study. The review resulted in a bibliography. Acquired information enabled the priority-ranking and selection of pesticides for project study and the identification of optimum solvents for liquid-liquid extraction. A compilation of various engineering design options for liquid-liquid extraction systems led to the selection of a design choice consisting of a countercurrent-flow rotary-disc contactor (RDC) process. Finally, literature on engineering design economics enabled the formulation of reliable cost estimates for the derived technology. The bench-scale RDC-type solvent extraction of organic pesticides (SEXOP) system was used to test both synthetic and real-world process effluent DDT samples. Tests using the synthetic sample demonstrated extraction efficiencies in excess of 99.9%. Subsequent to process optimization, bench-scale runs using real-world process effluent DDT samples (consisting of raw untreated waste) resulted in a cleanup for most constituents in excess of 99%. No constituents of the best-case final run were extracted at an efficiency level below 90%.

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Solvents	Process Streams	11K
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ABSTRACT

This cooperative agreement research program was initiated with the overall objective of determining the feasibility of extraction of pesticides from process streams using a liquid-liquid solvent extraction approach.

Initially, a brief literature review was conducted to provide foundational data in support of the technology identified for study. The review resulted in the compilation of a bibliography organized by subject area into four discrete categories consistent with the project goals. Information was acquired which enabled the priority ranking and subsequent selection of pesticides for project study and the identification of optimum solvents for liquid-liquid extraction. A compilation of various engineering design options for liquid-liquid extraction systems led to the selection of a design choice consisting of a counter-current flow, rotary disc contactor process. Finally, literature on engineering process economics enabled the formulation of reliable cost estimates for the derived technology.

Information from the literature review and collaboration with EPA personnel led to the selection of seven pesticides and five solvents for study. These pesticides and solvents were subjected to a comprehensive screening and extraction study to determine the partition coefficient (K_p), for each pesticide/solvent combination. The screening extraction study utilized a simple batch hand-shakeout procedure and resulted in the conclusion that solvent extraction, using high volatility/low water solubility solvents constituted a highly promising technique for pesticide effluent cleanup. Partition coefficients for the pesticide/solvent mixtures studied are presented in this report.

Based on the literature review and the screening extraction research, it was determined that the optimum design candidate for a liquid-liquid extraction device consisted of what is known as a rotating disc contactor (RDC). Based on this finding, S-CUBED elected to design and fabricate a bench-scale RDC-type system. The purpose of this system was to further test the hypothesis that Solvent Extraction of Organic Pesticides (SEXOP) from process streams would be commercially feasible both technically and economically. Subsequent to its fabrication the system was used to test both synthetic and real world process effluent DDT samples. Tests using the synthetic sample demonstrated extraction efficiencies in excess of 99.999...%. Subsequent to process optimization, bench-scale runs using real world process effluent DDT samples (consisting of raw untreated waste) resulted in a cleanup for most constituents in excess of 99%. No constituents of the best case final run were extracted at an efficiency level below 90%.

In light of the technical success of SEXOP with synthetic and process effuent DDT samples, an economic analysis of the process was undertaken to explore the possibility of attendant economic benefits. An effort was made (based on current knowledge) to project an engineering cost estimate for both a large and a small commercial-scale SEXOP process. The derived estimates were then compared to the more firmly established capital and operational costs associated with carbon adsorption technology. This comparison revealed that SEXOP technology compares favorably with the carbon adsorption alternative.

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1.0 INTRODUCTION

This report describes work accomplished under cooperative agreement research and development project (No. CR807346010) conducted between S-CUBED and the U.S. EPA, to explore the feasibility of extraction of pesticides from process streams using a liquid-liquid solvent extraction approach. Research conducted on the project was structured such that the following three areas were addressed:

1. Solvent-pesticide partition coefficients were established through use of both synthetic pesticide mixtures and pesticide manufacturing wastewaters.
2. A bench scale liquid-liquid extraction unit was designed and fabricated and experimental studies were conducted to test the capability of the system.
3. Subsequent to the bench scale runs, economic feasibility studies were conducted in order to determine the potential process viability as compared to commercial scale carbon absorption systems.

Research objectives in the above three areas were met through conduct of work in the following four discrete task areas:

Task 1 - Literature Review
Task 2 - Screening Extraction Studies
Task 3 - Bench Scale Studies
Task 4 - Economic Analysis

Foundational concepts and supportive data for work on this project were derived from prior in-house S-CUBED supported research into the feasibility of liquid-liquid solvent extraction of pesticides from water.

Sections 2 and 3 of this report present conclusions and recommendations respectively, Section 4 provides a comprehensive discussion of the research conducted in each of the above task work areas.

2.0 RESULTS AND CONCLUSIONS

Summarized herein are the conclusions derived from the four general project research objectives. These objectives involved: conduct of a literature review; derivation of partition coefficients for selected pesticides/solvent/water systems; the design, fabrication and checkout of a bench-scale extraction device; and the determination of economic feasibility for the developed solvent extraction technology. The conclusions for each of these three project research objectives are summarized separately below.

2.1 LITERATURE REVIEW

A brief literature review was conducted to establish current information on:

- Ranking of environmentally significant pesticides.
- Candidate solvent systems appropriate for liquid-liquid extraction.
- Engineering design parameters for a liquid-liquid extraction process.
- Economic considerations with respect to solvent selection and process design.

This literature review activity resulted in the compilation of a bibliography organized by subject area into the above four categories. The bibliography also provides a brief abstract along with each citation.

Information acquired during the course of the literature review provided strong foundational data in support of the identified project research objectives. These data enabled the priority ranking and subsequent selection of pesticides for project study and the identification of candidate solvents for liquid-liquid extraction. A compilation of various engineering design options for liquid-liquid extraction systems led to the selection of a suitable design choice consisting of a counter-current flow, rotary disc contactor process. Finally, literature on engineering process economics enabled the formulation of reliable cost estimates for the derived technology.

2.2 DERIVATION OF PARTITION COEFFICIENTS

The literature review, in conjunction with collaboration with EPA personnel, led to the selection of the following pesticides (the term pesticide throughout this report is used as a generic term which includes both insecticides and herbicides) and solvents:

- Pesticides
  - DDT
  - Chlordane
  - Norflurazon
  - Diuron
  - Bromacil
  - 2,4-D
  - Glyphosate

- Solvents
  - Hexane
  - Pentane
  - Isopropyl Ether
  - Diethyl Ether
  - Butyl Chloride

These pesticides and solvents were subjected to a detailed screening and extraction study designed to determine the partition coefficient (K_p) for each pesticide/solvent combination. The convention associated with the extractability of a constituent from water stipulates that a high K_p value strongly favors high extraction efficiencies. The screening extraction studies conducted during this phase of the project (using a simple batch, hand-shakeout procedure) confirmed the findings based on previous S-CUBED supported research, that solvent extraction, using high volatility/low water solubility solvents, constituted a highly promising technique for of the screening extraction studies were considered to be sufficient to warrent initiation of the Task 3 Bench Scale Studies.

2.3 DESIGN, FABRICATION AND CHECKOUT OF A BENCH-SCALE SOLVENT EXTRACTION PROCESS

Based on the literature review and the screening extraction research, it was determined that the optimum design category for a liquid-liquid extractor system belongs to a group of process types called "Continuous Differential Contactors". Within this design group, the most highly favored option consisted of what is known as a rotating disk contactor (RDC). Based on this finding, S-CUBED elected to design and fabricate a bench-scale RDC-type system. Comprehensive discussion, presenting both pictoral and narrative design information, is presented in this report.

The purpose of this bench-scale system was to test further the hypothesis that solvent extraction of organic pesticides (SEXOP) from process streams would be commercially feasible both technically and economically. Subsequent to fabrication of the bench-scale system, a series of 10 studies were conducted using both synthetic and real world process effluent DDT samples. Studies using the synthetic samples resulted in a cleanup (i.e., extraction efficiency) in excess of 99.9999......%. Subsequent to process optimization, bench-scale runs using a real world process effluent DDT sample resulted in a cleanup for most constituents in excess of 99%. No constituents in the sample (of the best-case final run) were extracted at an efficiency level below 90%. Data in support of these findings are presented in this report. It should be stressed that the process effluent samples consisted of raw untreated wastewater which Gas Chromatography/Mass Spectrophotometry (GC/MS) analysis revealed to contain at least 52 components. Based on the high extraction efficiencies resulting from the bench scale runs using DDT, and the generally favorable extraction coefficients for the pesticides examined during the screening extraction studies, it can be concluded that SEXOP technology is potentially applicable to other constituents with similar Kp values. An examination of the detailed chemical composition of available in-house effluent samples shows that many of the same constituents present in the DDT sample are common to other wastes as well. This would indicate a broad-range applicability of SEXOP to a variety of highly contaminated samples.

2.4 ECONOMIC ANALYSIS

In light of the technical results of SEXOP with the synthetic and process effluent DDT samples, an economic analysis of the process was undertaken to develop an economic basis for the technology. This was accomplished using a twofold approach: (1) based on current knowledge, an engineering cost estimate was projected for both a large and a small commercial-scale SEXOP process; and (2) these cost projections were compared with the more firmly established capital and operational costs associated with carbon adsorption technology. This study revealed that the cost of the SEXOP technology compares favorably with the carbon adsorption alternative. Current state-of-the-technology for SEXOP is such that this determination must be viewed with some latitude.

3.0 FEASIBILITY OF SOLVENT EXTRACTION FOR THE REMOVAL OF PESTICIDES FROM PROCESS STREAMS

This section provides background information on the approach used and the result derived from research into the feasibility of solvent extraction of pesticides from process streams. Research on this project was divided into four discrete task areas as follows:

Task 1 - Literature Review
Task 2 - Screening Extraction Studies
Task 3 - Bench-Scale Studies
Task 4 - Economic Analysis

The following discussion addresses the work conducted in each one of these task areas.

3.1 TASK 1 - LITERATURE REVIEW

A literature review was conducted at project initiation with approximately a two month term allocated for the bulk of the search and a low level of effort allocated over the remainder of the project to keep the file current. The purpose of the literature review was to acquire information in the following areas:

- Those pesticides manufactured in the United States which are the most environmentally significant either because of their high toxicity ranking or because they are manufactured in large quantities.
- Candidate solvent systems which can effectively be employed in continuous liquid-liquid extraction systems.
- Continuous liquid-liquid extraction engineering process designs.
- Economic considerations with respect to solvent selection and process design.

At the initiation of the literature review a special category was set aside for each of the above four areas of study. This resulted in the formulation of an annotated bibliography structured according to the following format:

- Subject category
- Reference in alphabetical order by author
- Brief bibliographic statement.

The bibliography resulting from this effort is presented at the conclusion of this report. The following discussion addresses key information sources which contributed significantly to the research conducted on this project in each of the four previously cited categories.

3.1.1 Ranking of Environmentally Significant Pesticides

The most significant literature source for this subject area is a report by Kelso, et al., (1.2). The report addresses the selection of relevant factors to evaluate the pollution potential from pesticides manufacturing and formulating operations and the need for developing emission control technology. A pesticide priority numerical rating system is devised for each of the following six measures of environmental significance:

1. Estimated 1974 production volume,
2. Acute mammalian toxicity (Oral LD_{50} rats),
3. Suspected carcinogenicity, mutagenicity, and/or teratogenicity,
4. Toxicity to fish, birds and invertebrates,
5. Persistence, and
6. Biomagnification, bioaccumulation and environmental mobility.

Each of the above criteria was assumed to be equally important in affecting the pollution potential of a pesticide, since there was no quantitative method available for weighing the importance of each of these criteria against one another. The numerical values assigned to each criterion were assumed to be additive to arrive at a total rate for each pesticide and each criterion was evaluated on a numerical scale of zero to four. Table 1 presents a comprehensive listing of the findings of this study for the 50 pesticides examined by the authors. Based on the Table 1 prioritized listings by Kelso, et al., and guidance from EPA concerning pesticides of special interest, Table 2 presents a prioritized listing of the eight candidate pesticides selected for study on this project and their associated severity ranking numbers. Glyphosate and Norflurazon were not examined in the study by Kelso, et al., however, they have been assigned ranking numbers of eight and seven, respectively, based on information derived from other literature sources.

3.1.2 Optimum Solvent Systems Which Can Effectively Be Employed In Continuous Liquid-Liquid Extraction Systems

Numerous literature sources addressing the use of solvent systems for liquid-liquid extraction of organic materials were studied. The majority of this literature addressed the issue of extraction of organic compounds from water, while only a small number of studies addressed the issue of pesticide extraction.

Voerman (1977) (2.23) conducted extractions from water using hexane and generated partition coefficients for six pesticides. Berosa and Boeman (1965) (2.4) similarly calculated Kp-values (fraction of solute partitioning into the oganic phase) for 16 pesticides, and compared five solvent systems, one of which was hexane.

Hexane was the dominant solvent of all the papers dealing with the extraction of organics from water. Mixed systems, alcohols and

Table 1

PROPORITY RANKING OF INDIVIDUAL SYNTHETIC ORGANIC PESTICIDES FOR DETAILED SOURCE ASSESSMENT

	Rank-Order Pesticide	Criteria and numerical rating						Total priority rating
		Total 1974 production	Acute mammalian toxicity	Special toxicity	Wildlife toxicity	Persistence	Bioaccumulation biomagnification, and mobility	
1.	DDT	4	2	4	3	4	4	21
2.	Chlordane	3	2	4	1	4	4	18
3.	Heptachlor	1	3	4	1	4	4	17
4.	Aldrin	3	3	0	2	4	4	16
5.	MSMA	4	3	4	0	3	2	16
6.	Endrin	1	4	0	3	3	4	15
7.	PCP and Sodium	4	3	4	1	3	0	15
8.	DSMA	3	1	4	0	3	2	13
9.	Toxaphene	4	2	0	2	2	2	12
10.	Lindane and BHC	1	2	0	1	4	4	12
11.	Parathion	3	4	0	4	0	1	12
12.	Methyl parathion	4	4	0	3	0	1	12
13.	Dinoseb	1	3	4	3	1	0	12
14.	Trichlorophenols	4	1	4	0	2	0	11
15.	Phorate	3	4	0	3	1	0	11
16.	Carbaryl	4	2	4	0	0	1	11
17.	Diazinon	3	2	0	3	1	1	10
18.	Disulfoton	3	3	0	3	1	0	10
19.	Fensulfothion	2	4	0	3	1	0	10
20.	Carbofuran	3	3	0	3	0	1	10
21.	Cacodylic acid	1	1	4	0	3	1	10
22.	Trifluralin	4	2	0	3	1	0	10
23.	Dyfonate®	1	4	0	3	1	0	9
24.	Captan	3	2	4	0	0	0	9
25.	Maneb	3	1	4	0	1	0	9
26.	Methomyl	3	3	0	3	0	0	9
27.	Aldicarb	1	4	0	4	0	0	9
28.	Monocrotophos	2	3	0	3	0	0	8
29.	Atrazine	4	1	0	0	2	1	8
30.	Simazine	3	1	0	0	3	1	8
31.	Endosulfan	1	3	0	1	2	1	8
32.	Monuron	1	1	4	0	2	0	8
33.	Silvex	1	1	4	0	1	0	7
34.	Malathion	4	1	0	1	0	1	7
35.	Merphos	1	2	4	0	0	0	7
36.	Carbofenthion	1	3	0	3	0	0	7
37.	Ronnel	1	1	4	1	0	0	7
38.	Dimethoate	1	2	4	0	0	0	7
39.	Maleic hydrazide	2	1	4	0	0	0	7
40.	Diuron	3	2	0	0	2	0	7
41.	Zineb	2	1	4	0	0	0	7
42.	Nabam	1	2	4	0	0	0	7
43.	Propazine	3	0	0	0	4	0	7
44.	Picloram	1	1	0	0	4	0	6
45.	Captafol	1	1	4	0	0	0	6
46.	Nitralin	1	1	0	3	1	0	6
47.	Bromacil	3	1	0	0	2	0	6
48.	2,4-D, acids, esters, and salts	4	2	0	0	0	0	6
49.	Methoxychlor	1	1	0	1	1	2	6
50.	DDVP	1	2	0	3	0	0	6

From G. L. Kelso et al. (Ref. 1.2)

Table 2

PRIORITY OF THE EIGHT PESTICIDES SELECTED FOR SEXOP STUDY

Order of Environmental Significance	Pesticide	Total Priority Rating[1]
1	DDT	21
2	Chlordane	18
3	Toxaphene	12
4	Glyphosate	8
5	Norflurazon	7
6	Diuron	7
7	Bromacil	6
8	2,4-D	6

---

[1] Based on the study by Kelso (1.2) and information from other literature.

ethers, were also prevalent. Webb (1977) (2.24) studied the selection of extraction solvents by comparing eight solvent systems. This study concluded that chloroform, methylene chloride-ether mixtures and methylene chloride constituted optimum choices for general purpose use.

For the purposes of the this project, methylene chloride was eliminated as a candidate solvent, due to its high solubility in water and its status as a priority pollutant.

The solvents S-CUBED has chosen as candidates for this project were selected on the basis of information derived from the literature; commercial availability; and polarity. With respect to this latter parameter, solvents representing a full range of polarities were chosen, ranging from the most polar to the least polar in the following order:

1. Butyl Chloride,
2. Isopropyl Ether,
3. Diethyl Ether,
4. Hexane, and
5. Pentane.

During the course of this study, each of these candidate solvents were evaluated as extraction media and two were selected for use in the bench-scale experiments.

3.1.3 Continuous Liquid-Liquid Extraction Engineering Process Design

In addition to the literature review, S-CUBED also made personal contacts with industry representatives with a view towards identifying useful liquid-liquid extraction engineeing designs. The leading authority in this area appears to be C. J. King, who has written a textbook (3.8) and several reports and articles on the various aspects of separation processes. A wide variety of other authors were also studied, however, the nature of separation processes they described are of the standard variety and do not differ significantly from those presented in reviews by Judson King.

Continuous liquid-liquid solvent extraction has found numerous industrial applications in both control technology and resources reclamation areas. Applications to date include:

- Acetic acid recovery from pulping plants using ketones, ethers, and esters as extracting solvents.
- Extraction of sulfur compounds from gasoline using a methanol/water solvent.
- Dehydration of acetic acid.
- Refining of vegetable oils and fats.
- Manufacture of fine chemicals and pharmaceuticals.
- Purification of recycled solvents in the plastics industries.
- Separation of aromatics from low-octane paraffins in gasoline using diethylene glycol as extraction solvent.
- Removal of phenol and related compounds from waste waters.
- De-oiling of quench waters from petroleum operations.

For all such applications solvent extraction has been documented to be both technically and economically feasible.

The SEXOP approach described in this report is unique, however, in that it utilizes high volatility, low (water) solubility solvents as extraction media. The solvent extraction media generally employed in commercial liquid-liquid extraction systems is much less volatile and usually considerably more soluble in the treated matrix. Examples of typical solvents used in industrial liquid-liquid extraction systems include nitrobenzene, cresol, phenol, furfural, and blends of benzol-sulfur dioxide. In such systems, extraction frequently takes place at elevated temperatures and steam stripping of the raffinate and/or extract may be required for solvent recovery or increased purification.

While the theoretical and technical aspects of this technology are highly refined on a commercial level, negligible consideration has been devoted to applications in control technology areas. This is partially due to the highly specialized nature of the solvents required and also to the costs and further environmental problems associated with steam stripping, and solvent reclamation. Also, very little attention has been given to the use of solvent extraction for removal of trace level constituents in process effluent streams.

The SEXOP approach attempts to address these issues through use of solvent systems which can be employed at ambient temperature and which can be stripped and recovered easily due to low water solubility and high volatility.

With respect to the engineering aspects of this study the optimum design category consists of a group of process types called "Continuous Differential Contactors". Within this design group, four primary options are available. These are:

1. Rotating Disc Contactor (RDC),
2. Spray Contactor,
3. Baffle Plate Contactor, and
4. Pulsed Sieve-Plate Contactor.

Each of these four continuous differential contactors utilizes a two phase counter-current flow technique wherein the material of greater density is introduced at the top of the extractor and the material of lesser density is introduced at the base of the extractor in order to produce maximum liquid-liquid contact as both solutions migrate in opposing directions through the extractor. During the course of this migration, various different internal media (plates, packings, rotating discs, etc.) are used to enhance liquid-liquid contact.

Based on all the literature reviewed, the most efficient of these four systems appears to be the RDC extractor. Based on these findings, S-CUBED elected to design a bench-scale RDC system for the conduct of the Task 3 Bench-Scale Studies. This device will be described in detail in Section 4.3 of this report.

3.1.4 Economic Considerations With Respect To Solvent Selection And Process Design

Literature specific to the economic considerations associated with the design and construction of solvent extraction devices is minimal; however, three detailed and infomative sources were acquired. In a book by C. P. Hanson (4.5) entitled "Recent Advances in Liquid-Liquid Extraction", the chemistry, economics and design aspects of extraction processes are discussed. Mulligan and Fox (4.8) present a general overview of advances in the solvent extraction, although nothing specifically relating to pesticides is presented. D. W. Uhl (4.11) developed and presented a standard procedure for cost analysis of pollution control operations. This report by Uhl presents guidelines which facilitate the choice of procedures open to the estimator and establishes factors to be used in the economic evaluation.

Each of these authors tend to stress those economic factors which have historically been the most prevalent in the economic evaluation of most processing systems. These factors are:

- Process effluent stream flow volume,

- Required flow volume of extraction solvent,
- Commercial availability and cost of extraction solvent,
- Recoverability of extraction solvent based on volatility and solubility in water,
- Utility costs, and
- Operation costs, including labor and maintenance.

Most of the literature reviewed in this area indicates that the preferred method for conducting economic analyses on potential processing systems consists of breaking the operation down into discrete modules and subsequently summing individual criteria associated with each module.

Work conducted in this subject area by the above-cited authors also indicates that where liquid-liquid extraction is concerned, a major cost consideration in the economic analysis involves the reclamation and reuse of extraction solvent. It is important to note, however, that these authors have been primarily concerned with extraction systems for removing high concentrations of organics from refinery and chemical manufacturing streams. As stated earlier in Section 4.1.3, the solvents used in commercial systems tend to require elevated temperatures for steam stripping and quantitative solvent recovery is often difficult due to the solubility of the solvent in the material being treated. Also, commercial liquid-liquid extraction systems are often used to treat exclusively organic matrices such as in the example of diethylene glycol extraction of catalytic reformates for the recovery of aromatics.

In contrast, the SEXOP process utilizes high volatility/low solubility solvents in a predominantly aqueous medium. High volatility allows solvent stripping and recovery at ambient temperature and low solubility further minimizes solvent loss and process energy/material requirements. For these reasons, it is expected that while reclamation and reuse of solvent is a major economic consideration in existing liquid-liquid extraction systems, cost associated with this parameter would be considerably less with SEXOP.

3.2 TASK 2 - SCREENING EXTRACTION STUDIES

Based on information derived from the Task 1 Literature Review, the solvents and pesticides identified as experimental candidates were procured for screening extraction studies. A list of pesticides and commercial suppliers is presented in Table 3. As stated previously, the solvents chosen for study are: hexane, pentane, isopropyl ether, diethyl ether, and butyl chloride.

The central focus of the screening extraction studies pertains to a parameter called the "partition coefficient". The partition coefficient constitutes the primary consideration in whether a solvent extraction process will be effective. This partition coeficient, Kp, is defined as:

$$K_p = \frac{(S_B)_O}{(S_B)_W} \qquad (1)$$

where:

S_B is the solubility of the pollutant in the phase noted by the subscript O for organic and W for aqueous. The formula is an idealized extension of Henry's Law which states that at sufficiently high dilution in a liquid solution, the fugacity of a nondissociating solute becomes proportional to its concentration. With respect to Kp, it may then be said that the concentrations of any singular molecular species in two phases which are in equilibrium with one another will bear a constant ratio to each other. This constant ratio will hold

Table 3

PESTICIDES STUDIED DURING THE TASK 2 SCREENING EXTRACTION EXPERIMENTS

Pesticide (Commercial Name)	Chemical Name	Chemical Formula	Source
DDT	2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane	$C_{14}H_9Cl_5$	Montrose Chemical Corp. Torrance, CA
Chlorodane	1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{10}H_6Cl_8$	Veliscol Chemical Marshall, IL
Norflurazon	4-chloro-5(methylamino)-2-(a,a,a-trifluoro-m-tolyl)-3-(2H)-pyridazinone	$C_{12}H_9ClF_3N_3O$	Vertac West Memphis, AR
Diuron	3-(3,4-dichlorophenyl)1,1-diemthylurea	$C_9H_{10}Cl_2N_2O$	E.I. Du Pont de Nemours La Porte, TX
Bromacil	5-bromo-3-sec-butyl-6-methyluracil	$C_9H_3BrN_2O_2$	E.I. Du Pont de Nemours La Porte, TX
Toxaphene	Mixture of chlorinated camphenes		Hercules Chemical Brunswick, GA
2,4-D	2,4-dichlorophenoxy acetic acid	$C_8H_6Cl_2O_3$	Rodia Portland, OR
Glyphosate	N-(phosphonomethyl)glycine	$C_3H_8PNO_5$	Monsanto Company Luling, LA

true, provided that the activity coefficients remain relatively constant.

It must be stressed that the above is a simplified idealization which assumes no significant solute - solute interactions as well as no strong specific solute - solvent interactions. A variety of empirical studies (conducted both by S-CUBED and by other researchers) have shown that many organic compounds deviate considerably from ideal behavior in water and various solvents. Although this deviation from ideal behavior often precludes a quantitative determination of Kp, it is, nevertheless, useful as a qualitative indicator. This project, for example, utilizes the theoretical Kp (vis a vis the empirically determined Kp) as a tool to aid in the selection of optimum solvent/pesticide systems as candidates for use during SEXOP runs. These theoretical Kp's were determined by conducting a series of "screening extraction studies". In the screening extraction studies, solubilities were determined by mixing an excess amount of solute in an appropriate quantity of solvent to establish equilibrium between the solid and the resultant liquid phase at ambient temperatures (e.g., 22°C). These studies were accomplished by setting up a number of solubility vessels and agitating their contents for a minimum of 24 hours. After the desired contact time, the flask was allowed to stand to permit settling of the solid phase. An aliquot of the solution was removed, weighed and evaporated to dryness to determine the quantity in solution gravimetrically.

The extraction studies were conducted using a single batch storage extraction of water containing a known quantity of dissolved pollutant under investigation. The organic phase was then isolated and the quantity of pollutant extracted was determined using electron capture gas chromatography (ECGC). The resulting ECGC data was compared to the pollutant concentration in the aqueous phase and the partition coefficient for each solvent system was then calculated.

The laboratory procedures used during the conduct of the Task 2 Screening Extraction Studies are presented in Appendix B of this report. A summary of the results for this project activity are presented in Tables 4 through 7. Backup data for these determinations are available on file at S-CUBED, however, these tabulations are voluminous and therefore have not been included in this report.

For DDT, 2,4-D, chlordane, and toxaphene, it appears that the partition coefficients are relatively high and, hence, extraction into organic solvents is highly favored. Pesticides norflurazon, diuron and bromacil have relatively low K_p values. The pesticide least likely to be extracted effectively is glyphosate which has a very low K_p value for all solvents tested.

These partition coefficient data were reviewed in order to select the most promising solvent/pesticide combinations for use in the Task 3 Bench-Scale Studies. The rationale associated with this selection process is discussed below.

In choosing a solvent for a liquid-extraction process, there are frequently conflicting factors and certainly no single substance would ordinarily possess every desirable characteristic. The most desirable solvent for extracting one component of a solution in preference to another would dissolve a maximum of one component and a minimum of the other. The high K_p value for the pollutant/solvent/water system is desirable for any commerical extraction process in order to minimize the quantity of organic solvent that is used to extract the pollutant. Low flammability is, of course, desirable for reasons of safety. Other criteria to be considered are:

1. Solubility of the solvent in water.
2. Solvent boiling point.
3. Solvent cost.

Table 4

PESTICIDE SOLUBILITY IN SOLVENTS

(conc. im ppm)

SUMMARY

	Hexane	Pentane	Isopropyl Ether	Ether	Butyl Chloride
D D T	78,800	67,961	58,630	238,894	92,763
Chlordane	4,585	11,000	35,373	56,142	100,040
Norflurazon	223	454	1,040	3,189	3,319
Diuron	86	73	1,294	4,414	2,311
Bromacil	950	926	7,672	13,000	20,583
Toxaphene	20,604	11,000	57,924	49,883	45,788
2,4-D	144	116	50,905	39,966	3,445
Glyphosate	2,360	59	1,008	2,303	630

Table 5

SOLUBILITY OF PESTICIDES IN WATER (ppm)

DDT	0.25
Toxaphene	0.28
Chlordane	0.42
Norflurazon	17.0
Duiron	24.3
2,4-D	607
Bromacil	717.7
Glyphosate	21,200

Table 6

PARTITION COEFFICIENT, K_p, OF PESTICIDES

	Hexane	Pentane	Isopropyl Ether	Diethyl Ether	Butyl Chloride
DDT	320,000	270,000	230,000	960,000	370,000
Toxaphene	74,000	39,000	140,000	180,000	160,000
Chlordane	11,000	26,000	84,000	130,000	240,000
Norflurazon	17	27	61	190	200
Diuron	3.5	3.0	53.3	182	95.1
2,4-D	.02	.19	84	65.9	5.7
Bromacil	1.32	1.29	10.7	18.1	28.7
Glyphosate	0.111	0	0.048	0.109	0.030

Table 7

LOG K_p VALUES OF PESTICIDES

	Hexane	Pentane	Isopropyl Ether	Diethyl Ether	Butyl Chloride
DDT	5.50	5.43	5.37	5.98	5.57
Toxaphene	4.87	4.59	5.13	5.25	5.21
Chlordane	4.04	4.42	4.93	5.13	5.38
Norflurazon	1.12	1.43	1.79	2.27	2.29
Diuron	0.55	0.48	1.73	2.26	1.98
2,4-D	-1.7	-.72	1.92	1.82	.76
Bromacil	0.12	0.11	1.03	1.26	1.46
Glyphosate	-0.95	-2.56	-1.32	-0.96	-1.53

A comparative matrix considering these various parameters is presented in Table 8. Viewing Table 8, the kind of tradeoffs required in the solvent selection process become readily apparent. While n-butyl chloride is an excellent solvent from the standpoint of water solubility and K_p value, the boiling point is high and the cost in $/gallon is relatively high. Both of the ethers have attractive K_p values and costs, but water solubilities are high and the ever present danger of peroxide formation and explosion constitutes a substantial safety consideration. Even so, isopropyl ether still constitues a viable candidate at least for the purposes of the bench-scale feasibility studies.

Considering all of the solvents selected for study on this project, hexane probably represents the best overall compromise. Its water solubility and cost are both low, most K_p values are on the high end of the range, and the boiling point (while higher than would be desired for optimum conditions) is tolerable.

Based on the information derived from the Task 2 Screening Extraction Studies the selection of constituents for use during the Task 3 bench-scale runs was based on the above determinations. A decision was made (in collaboration with the EPA Project Officer) to begin the bench-scale runs with DDT/isopropyl ether as an optimum case scenario. In the event that problems (safety or otherwise) should develop with isopropyl ether, hexane would be substituted as the extraction solvent. The results of the Task 3 bench-scale activity are presented in the following subsection.

3.3 TASK 3 - FABRICATION OF THE BENCH-SCALE DEVICE AND CONDUCT OF EXPERIMENTAL PROCESS SAMPLE RUNS

During this phase of the project, the bench-scale device was fabricated and checkout runs were conducted using the candidate solvents and pesticides selected as a result of the screening

Table 8

CRITERIA USED FOR THE SELECTION OF SOLVENT FOR THE BENCH-SCALE STUDY

Solvent	Solubility in Water (Percent)	Boiling Point (°C)	$/Gal	Kp (Theoretical Value)			
n-Butylchloride	0.02	78.4	3.20	DDT	370,000	Diuron	95.1
				Toxaphene	160,000	2,4-D	5.7
				Chlordane	240,000	Bromacil	28.7
				Norflurazon	200	Glyphosate	0.03
Isopropyl Ether	0.2	68	2.50	DDT	230,000	Diuron	53.3
				Toxaphene	140,000	2,4-D	84
				Chlordane	84,000	Bromacil	10.7
				Norflurazon	61	Glyphosate	0.048
Hexane	0.03	69	2.40	DDT	320,000	Diuron	3.5
				Toxaphene	74,000	2,4-D	0.02
				Chlordane	11,000	Bromacil	1.32
				Norflurazon	17	Glyphosate	0.111
Pentane	0.01	36	3.00	DDT	270,000	Diuron	3.0
				Toxaphene	39,000	2,4-D	0.19
				Chlordane	26,000	Bromacil	1.29
				Norflurazon	27	Glyphosate	0
Diethyl Ether	6.9	34.5	2.70	DDT	960,000	Diuron	182
				Toxaphene	180,000	2,4-D	65.9
				Chlordane	130,000	Bromacil	18.1
				Norflurazon	190	Glyphosate	0.109

extraction studies discussed in the previous subsection. These checkout runs consisted of experiments using synthetic DDT solutions and real world process effluent samples. All activities concerning bench-scale process fabrication and experimental checkout runs are addressed separately in the following discussion.

3.3.1 Fabrication Of The Bench-Scale Device

Based on the literature review effort described earlier in Section 4.1, the optimum design category for liquid-liquid extraction systems was found to consist of a group of process types called "Continuous Differential Contactors". All differential contactor designs utilized a two phase counter-current flow technique wherein the material of greater density is introduced at the top of an extractor unit and the material of lesser density is introduced at the base. In this fashion maximum liquid-liquid contact is obtained as both solutions migrate in opposing directions through the extractor unit.

Based on all the literature reviewed, it was S-CUBED's best engineering judgement that an extractor design of the rotary disc contactor (RDC) variety would provide maximum extraction efficiencies. The engineering design for this extractor was illustrated schematically in Section 4.1 of this report. Below, a detailed discussion of the various components which comprise the overall Solvent Extraction of Organic Pesticides (hereafter called SEXOP) process is presented. This discussion is supplemented by labled photographs of the various SEXOP components.

Figure 1 illustrates the fully assembled RDC with the rotary disc shaft and stator ring cluster removed for viewing. The outer shell is a stainless steel (SS) pipe four-feet in length and three-inches in diameter. The motor is mounted about one foot above the top end plate of the RDC. Ball-bearings support the shaft just

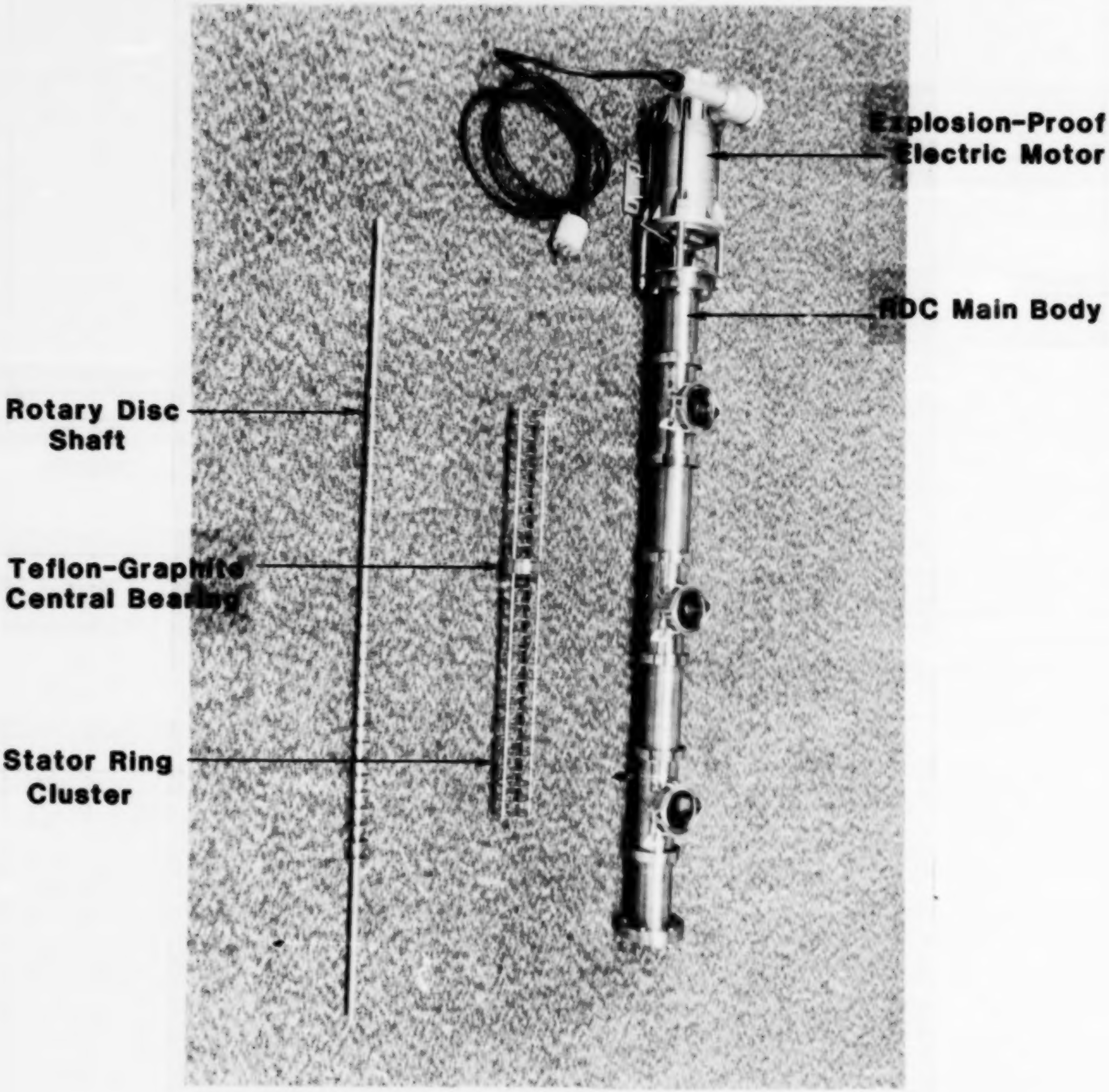


Figure 1 Fully Assembled RDC With Rotary Disc Shaft And Stator Rings Removed

above the flexible coupling which connects the motor shaft to the RDC shaft. The motor is connected with a variable speed controller in order to permit a variable range rotational speed with a maximum of 1750 rpm. The stator ring cluster, also shown in Figure 1, consists of a series of rings which are 0.035-inch thick with an outside diameter slightly less than the three-inch inside diameter of the RDC shell. The stator centerline holes are two inches in diameter. The stators are held in position by three 3/16-inch rods running the entire length of the column. One inch spacers are used to separate the stators, and threaded tightening nuts are used at each end of the rods. A mid-column bearing is installed to minimize vibration of the rotating shaft. The bearing is held in position by the three 3/16-inch rods.

The rotary discs, shown on the far left of Figure 1, are 0.035-inch thick with a diameter of 1.5 inches and and 0.5-inch centerline hole bored such that they just slide along the 0.5-inch-diameter rotating shaft. The discs are held firmly in position by a threaded tightening nut at one end, a fixed sleeve at the other end, and one-inch lengths of tubing which act as spacers to separate each disc.

Figure 2 illustrates the same assembly as did Figure 1 except that in Figure 2, the RDC is completely disassembled to show all component parts. Glass discs covering the viewports are three inches in diameter and 1/8 inch in thickness. They are assembled with metal as well as Teflon gaskets and cinch clamps. Also shown in Figure 2, are stationary tubular shields surrounding the rotation shaft and extending nine inches from each end plate of the RDC to reduce turbulence in these quiescent zones. The solvent enters from the bottom end plate through a length of 0.25-inch-diameter tubing which carries it into the area between the rotating shaft and the staionary tubing. A short length of Teflon tube was attached to the top of the bottom stationary shield. Since the Teflon is preferentially wetted

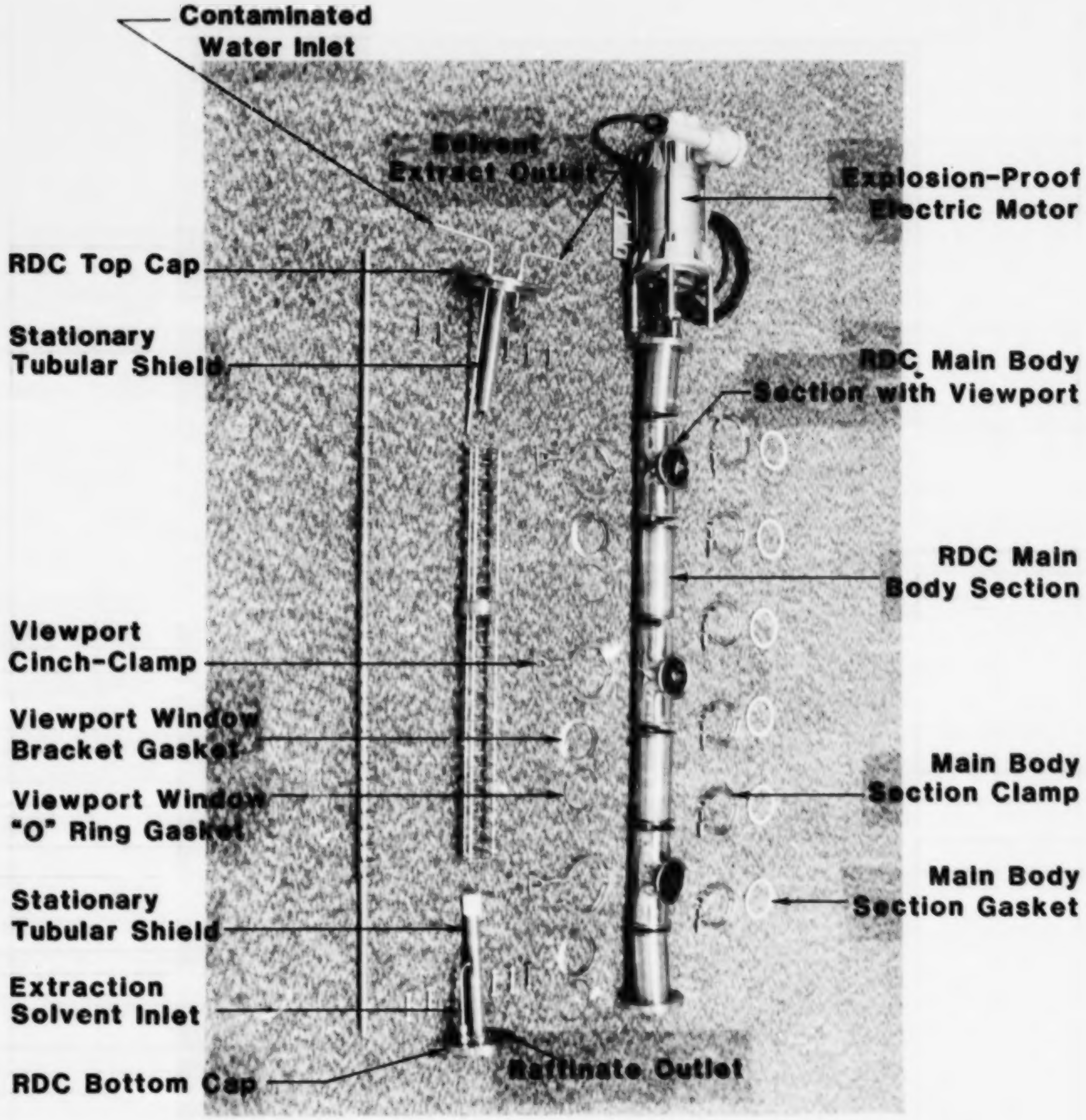


Figure 2 Fully Exploded View Of The RDC

by the solvent (i.e., displays what is known as a "wetted-wall column" characteristic), a thin film of solvent is emitted so that the shearing action of the bottom disc allows dispersion into small droplets.

Figure 3 illustrates the counter-current solvent stripper which, when fully assembled, is four feet in length and three inches in diameter. It is composed of assembly sections one foot in length to increase or reduce the total length, as needed, depending on efficiency conditions during the experiment. The packed bed of the column consists of 6-mm glass beads to simulate the packings used in commercial-scale strippers (Figure 4). This will provide a larger surface area with sufficent void space to permit efficient liquid and inert gas (nitrogen) counter current flow.

Nitrogen and solvent vapor emitted from the top of the stripping column are introduced into a multiple-loop water/air condensor which is made of 0.5-inch SS tubing. The condensed solvent is accumulated in a collection basin which is also made of stainless steel (Figure 5). Reclaim solvent from the collector is recirculated to the RDC.

Figures 6 through 10 depict varying different views of the RDC SEXOP system assembled in a large walk-in hood located in the S-CUBED chemical engineering laboratory. The walk-in hood, which houses the bench-scale system has a maximum flow capacity of 2,125 cfm. It is constructed entirely of explosion proof materials with shatter proof sliding glass doors on both sides. All electrical switching components including the pumping station shown in Figure 10, are located externally as a safety measure.

3.3.2 SEXOP Runs Using Synthetic DDT Solutions

Following fabrication of the bench-scale SEXOP device, preliminary checkout runs were conducted to insure operability of the

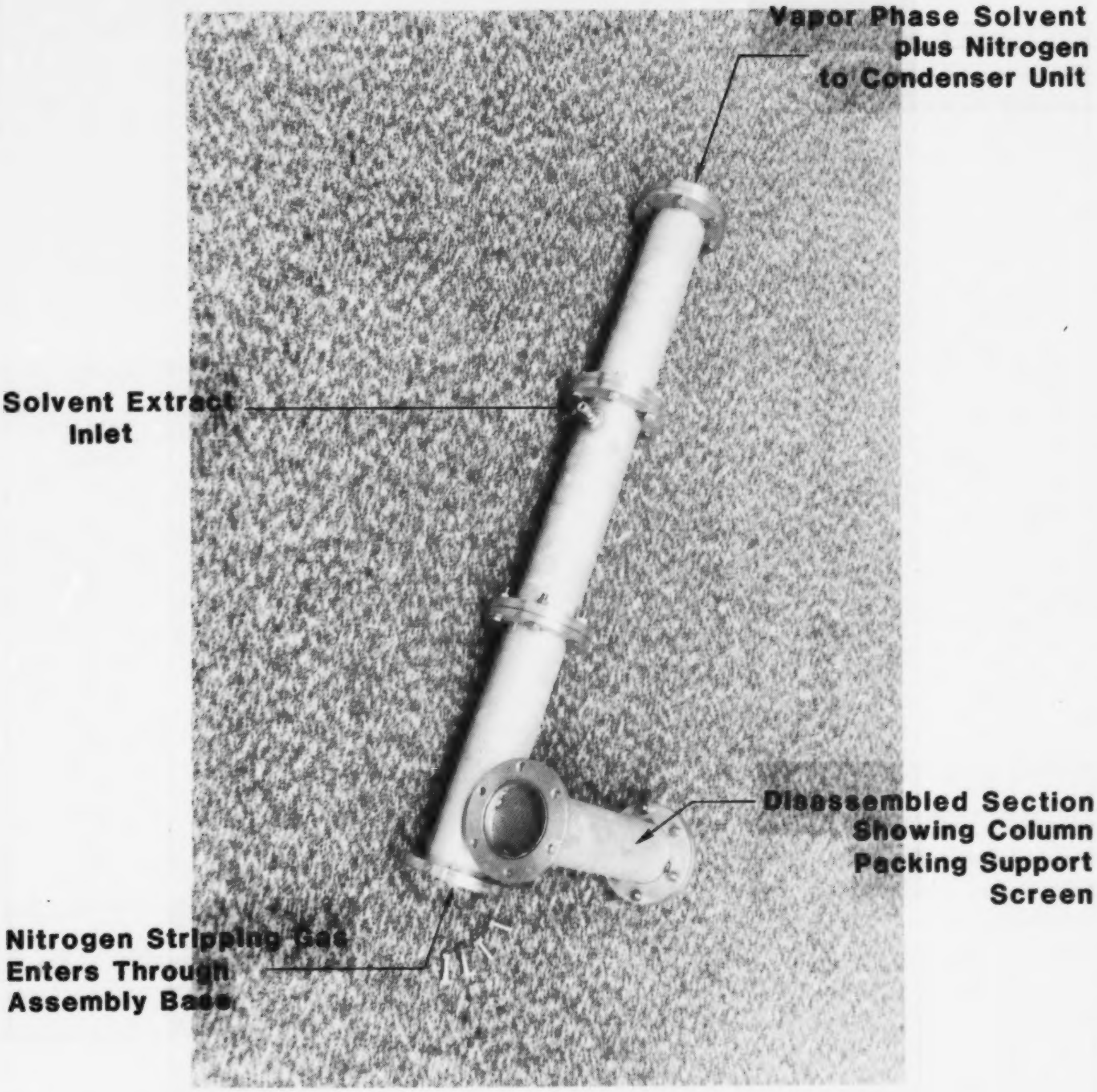

Vapor Phase Solvent plus Nitrogen to Condenser Unit
Solvent Extract Inlet
Disassembled Section Showing Column Packing Support Screen
Nitrogen Stripping Gas Enters Through Assembly Base

Figure 3 Counter-Current Solvent Stripper Shown With One Section Of The Assembly Detached

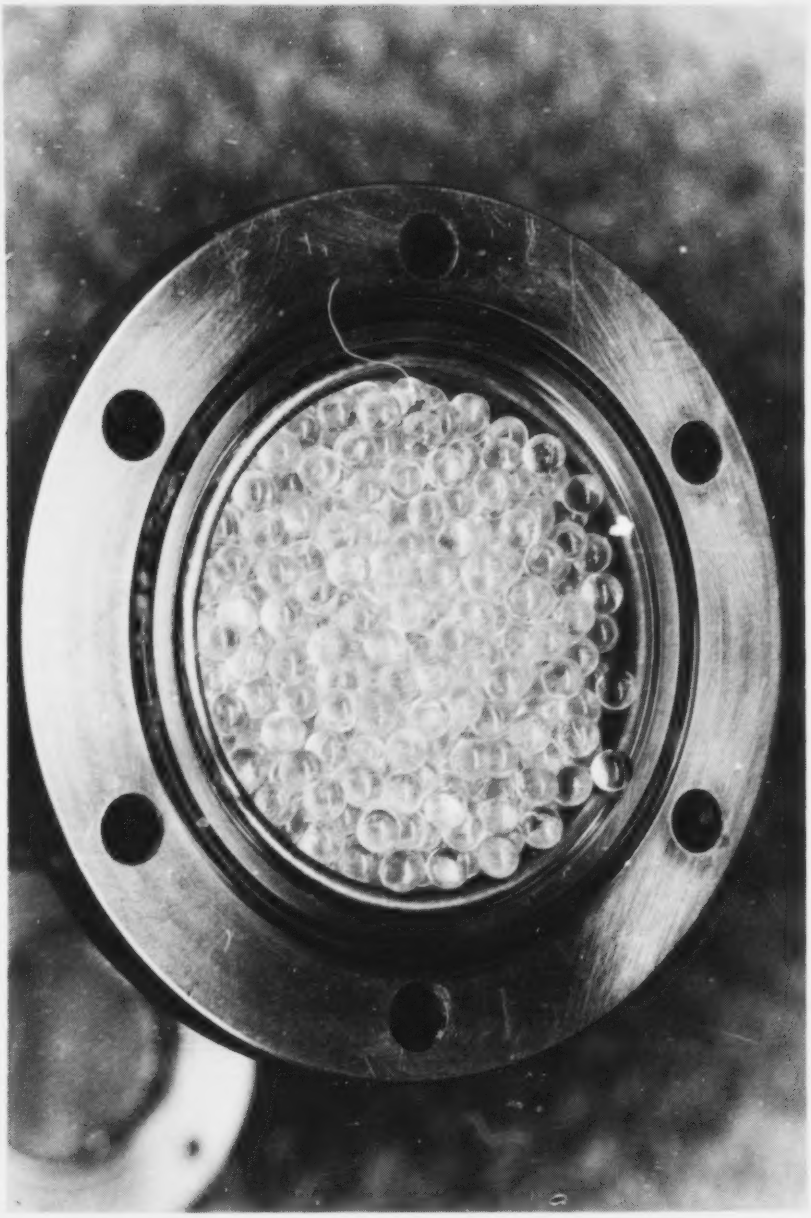


Figure 4 One Section Of The Counter-Current Stripper Column Filled With Glass Bead Packing

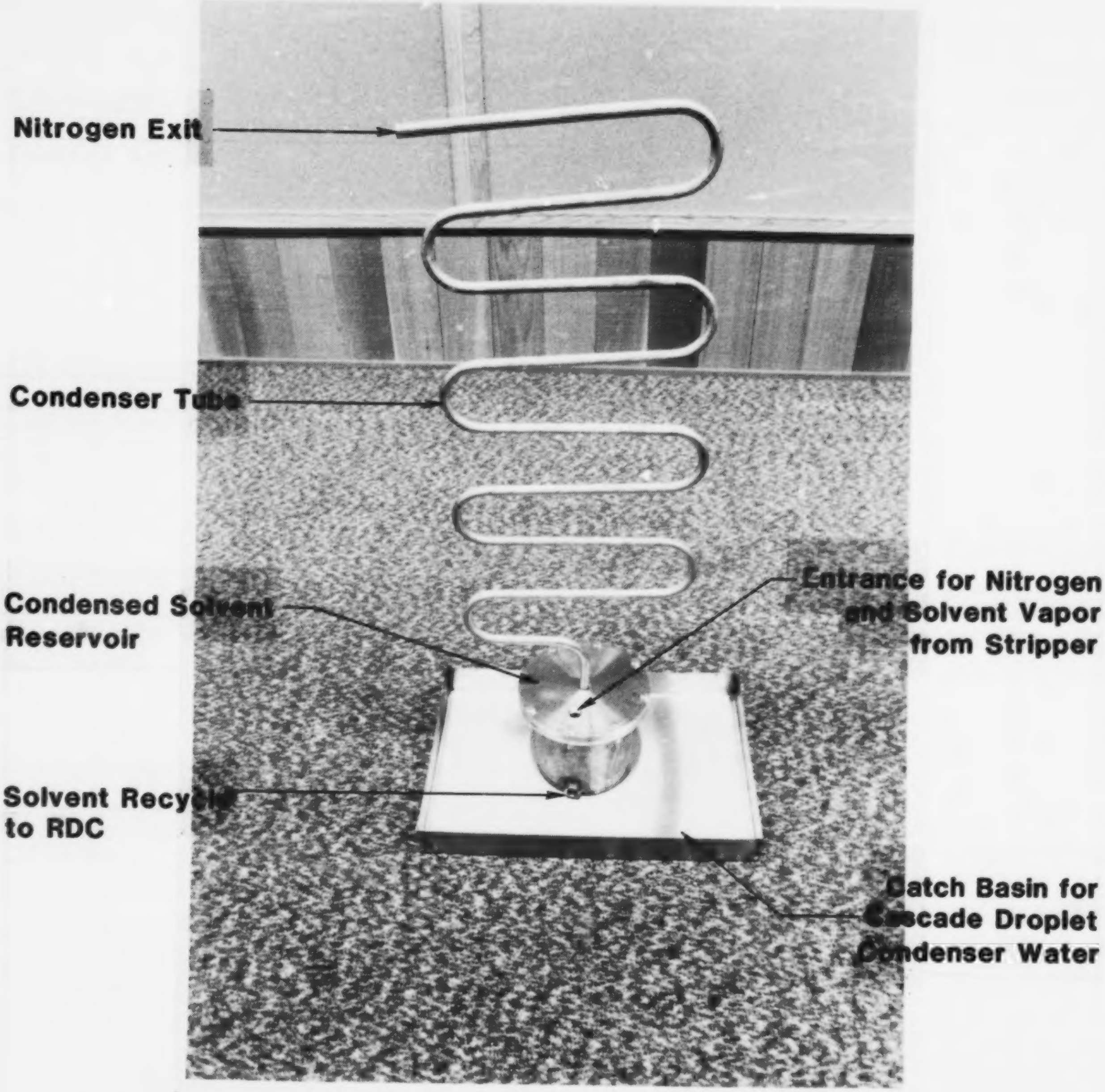

Nitrogen Exit
Condenser Tube
Condensed Solvent Reservoir
Entrance for Nitrogen and Solvent Vapor from Stripper
Solvent Recycle to RDC
Catch Basin for Cascade Droplet Condenser Water

Figure 5 Condenser Unit

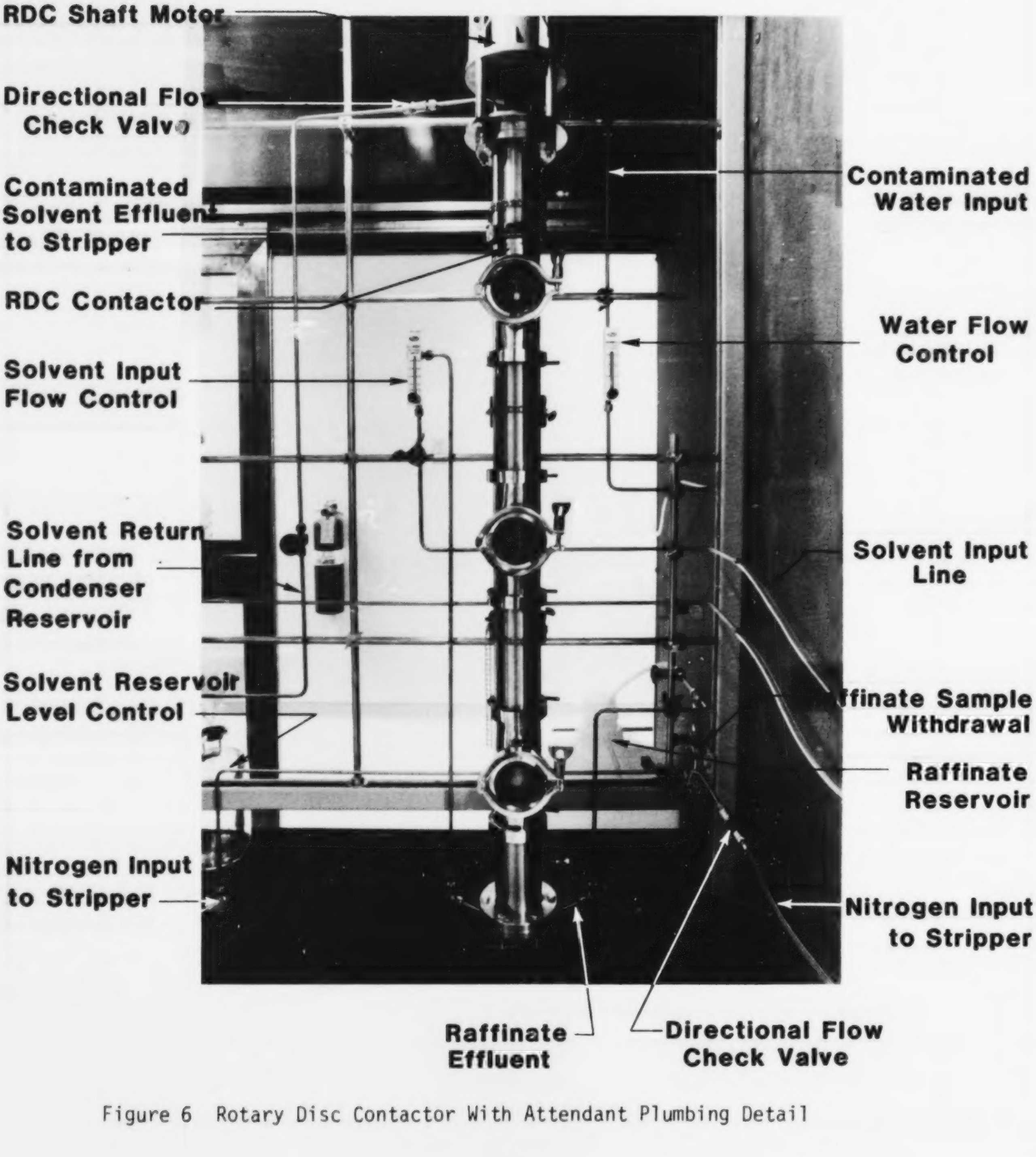

RDC Shaft Motor
Directional Flow Check Valve
Contaminated Solvent Effluent to Stripper
RDC Contactor
Solvent Input Flow Control
Solvent Return Line from Condenser Reservoir
Solvent Reservoir Level Control
Nitrogen Input to Stripper
Contaminated Water Input
Water Flow Control
Solvent Input Line
ffinate Sample Withdrawal
Raffinate Reservoir
Nitrogen Input to Stripper
Raffinate Effluent
Directional Flow Check Valve

Figure 6 Rotary Disc Contactor With Attendant Plumbing Detail

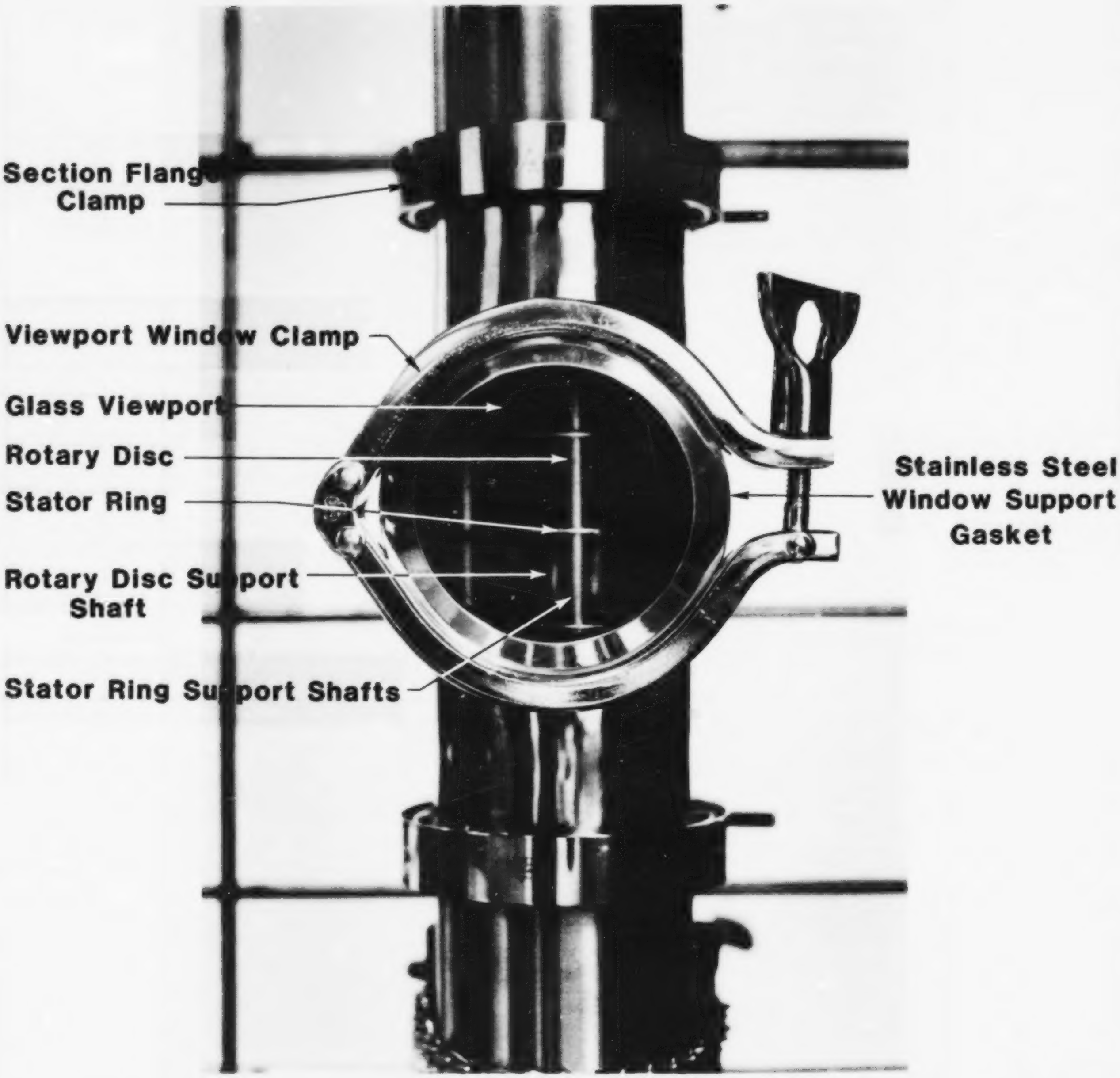

Section Flange Clamp
Viewport Window Clamp
Glass Viewport
Rotary Disc
Stator Ring
Rotary Disc Support Shaft
Stator Ring Support Shafts
Stainless Steel Window Support Gasket

Figure 7 Closeup View Of The Rotary Disc Contactor

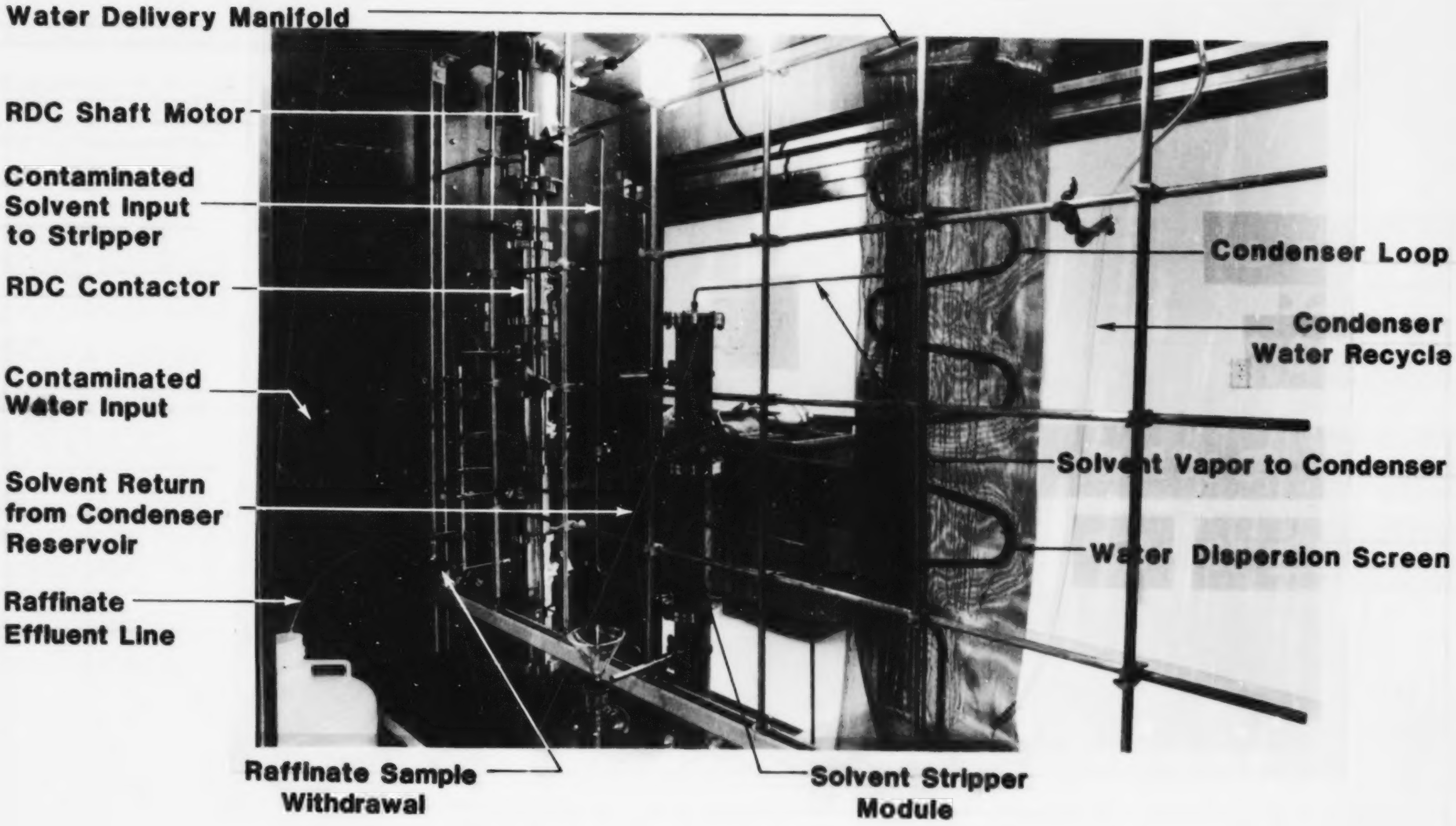


Figure 8 Complete Bench-Scale Unit - Rear Detail Of The Assembly

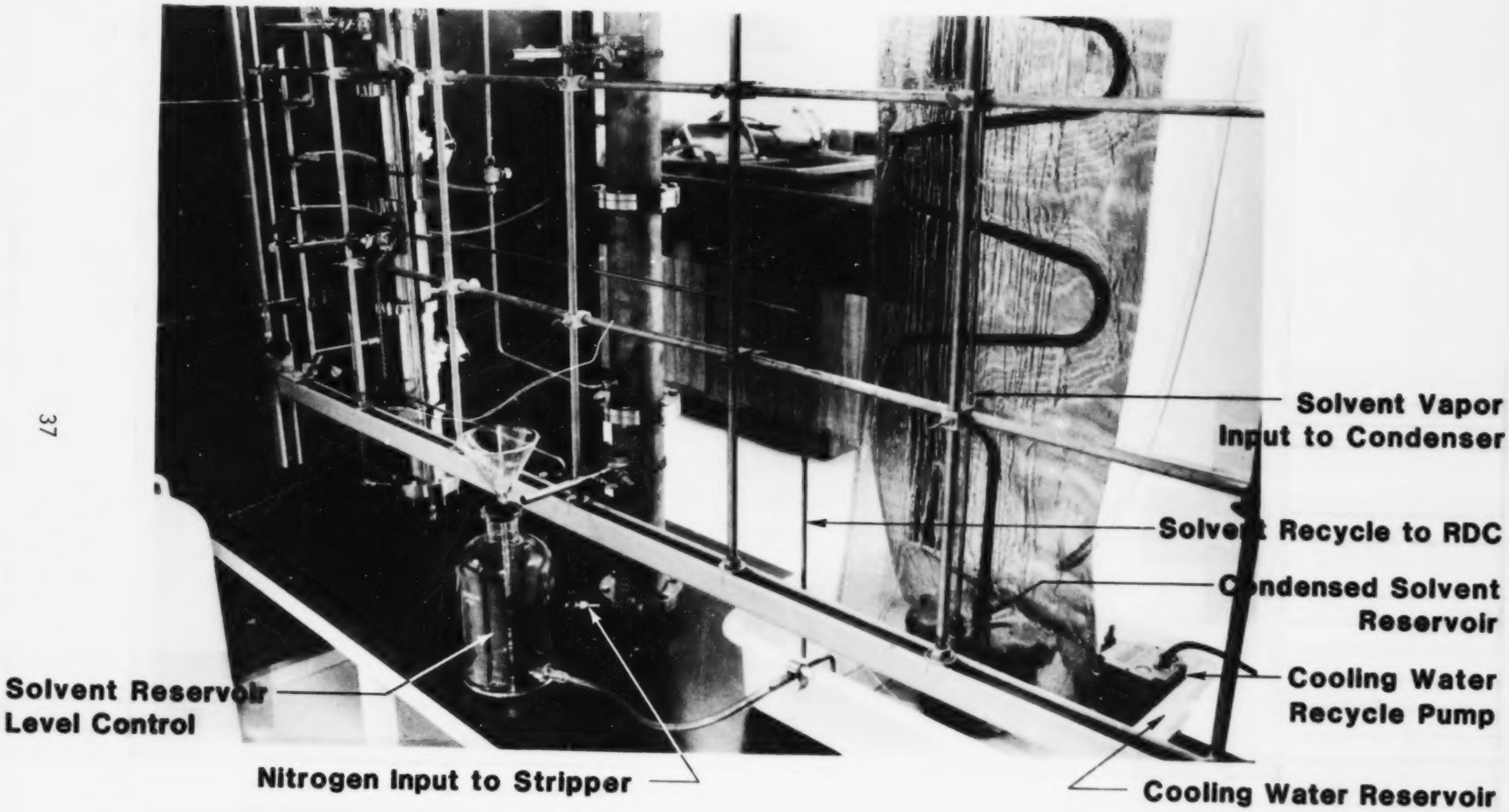

Solvent Vapor Input to Condenser
Solvent Recycle to RDC
Condensed Solvent Reservoir
Cooling Water Recycle Pump
Cooling Water Reservoir
Nitrogen Input to Stripper
Solvent Reservoir Level Control

Figure 9 Complete Bench-Scale Unit With Rear View Plumbing Detail

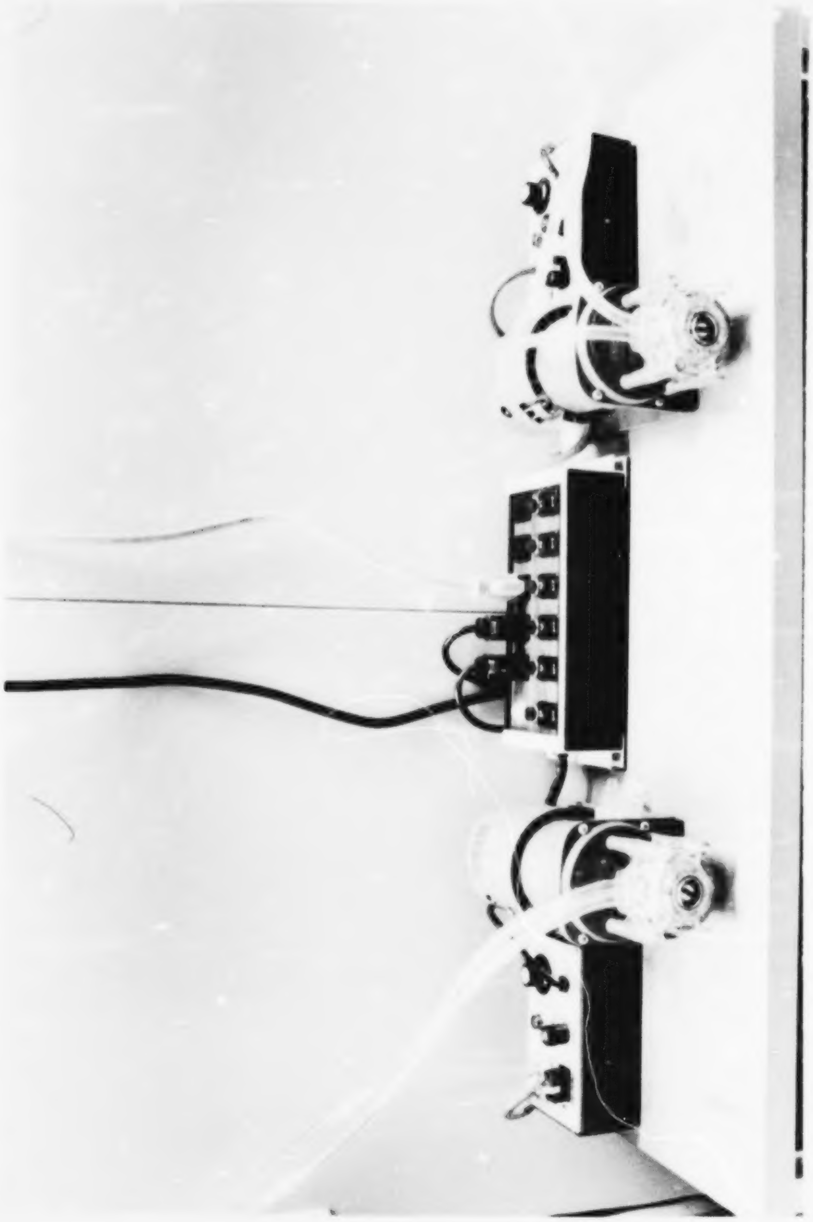


Figure 10 Pumping And Electrical Control Station Mounted Externally To Walk-In Hood

integrated system as a whole. A typical checkout run involved the following parameters:

1. Preparing and charging the water as well as solvent to the feed tanks,
2. Initializing flows in a specific manner that would insure smooth operation and rapid approach to steady state,
3. Allowing sufficient time to reach steady state,
4. Collecting final samples and recording measured flow rates, temperatures, etc. and,
5. Terminating flows in a manner that would leave all fluids in one or another of the tanks with all other equipment empty.

Between experiments, all parts of equipment which came in contact with pollutant-containing fluids were cleaned by water and acetone, followed by water washing. A more detailed discussion of the checkout procedure is presented in Appendix A.

Once the process checkout phase was complete and operational integrity was assured, the next step in the research plan involved the conduct of SEXOP runs using synthetic saturated DDT solutions. These solutions were formulated in 10 gallon batches and were used to simulate extractor feedstock until the full volume was depleted through the course of one or more runs. Individual runs were of from 2 to 3 hours in duration and the exchange rate per hour (i.e., full RDC column volume exchange) ranged from about 1.4 to 3.5. The total RDC column volume is 1.27 gallons (4.8 liters). The specific volume selected for the exchange rate per hour for a given run was a function of other run parameters and as such, constituted one of the experimental variables. The list of experimental variables pertinent to each SEXOP run is as follows:

- Rotary disc shaft motor speed
- Nitrogen stripper flow

- Solvent-to-water ratio
- Number of RDC column volume exchanges per hour.

For the purpose of research performed during this Task 3 activity, the above experimental variables were used to formulate standardized engineering run sheets. These run sheets were then used for all subsequent bench-scale experiments performed throughout the remaining duration of the project. Once the previously discussed checkout runs were conducted and the engineering run sheets were formulated, the initial bench-scale run using the saturated synthetic DDT sample was performed.

The purpose in conducting the initial bench-scale run was to establish a set of baseline parameters which could be used in future runs to optimize process controls, thereby deriving maximum efficiency from the system. For this reason, the initial process run was conducted using worst case run conditions, in order that the effects of run paramter optimization could be observed during future runs.

Operating conditions for the first bench-scale run are shown on the engineering flow sheet presented as Table 9. Viewing Table 9, it can be seen that the rotary disc shaft motor speed is on a relatively low setting (the full range setting is 100) and the RDC column exchange rate (3.5 full volume exchanges per hour) is relatively high at a water to solvent ratio of 10:1. The solvent used for this first run was isopropyl ether. During the course of future runs the variables shown on the Table 9 engineering flow sheet were manipulated in varying different combinations in order to optimize run efficiency. For example, an increase in the motor speed will increase turbulence, decrease solvent droplet size and increase solvent-to-water surface area exposure, thereby enhancing the extraction efficiency. Alternatively, a decrease in the solvent and water flow rates will lower the solvent exchange rate, thereby increasing residence time and subsequently enhancing extraction efficiency.

Table 9

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 001
DATE 8/09/81
DESCRIPTION Synthetic DDT

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
Start Material	10:30					850		3,890		
T_0	10:45	70	8	700	25	850	250	3,890	10:1	3.5
T_1	11:15	70	8	600	25	1,600	250	11,390	10:1	3.5
T_2	11:45	70	8	500	25	2,350	250	18,890	10:1	3.5
T_3	12:15	70	8	400	25	3,100	250	26,390	10:1	3.5
T_4	12:45	70	8	300	25	3.850	250	33.890	10:1	3.5
T_5	1:15	70	8	200	25	4,600	250	41,390	10:1	3.5
T_6	1:45	70	8	100	25	5,350	250	48,890	10:1	3.5

Comments: [1] Control box speed setting represents mid range speed.
[2] Isopropyl ether.

Viewing again the Table 9 engineering flow sheet, it can be seen that sample aliquots were acquired throughout the course of the run at 30 minute intervals. Both the starting material and run sample aliquots (T_0 through T_6) were analyzed gas chromatographically using standard EPA procedures (see Appendix B for specific protocols). These standard EPA procedures involved a hexane/methylene chloride solvent extraction of the aqueous aiquot followed by a Kuderna Danish concentration and electron capture gas chromagraphic (ECGC) analysis. Chromatograms for all first-run sample analyses are presented in Appendix C of this report. Viewing the Appendix C chromatograms, it can be seen that a number of early peaks in the 0-5 minute retention time range become progressively more significant in T_0 through T_6. Subsequent review of these data revealed that this characteristic was caused by first-run contamination artifacts.

The result of this analytical work is presented in Table 10 which lists the retention time for each of the peaks identified for comparative ratioing, along with their attendant peak areas. T_n represents the sum of the peak areas for DDT and its associated isomers. Viewing Table 10, it can be seen that values are provided for both raffinate concentration and extraction efficiency. These preliminary data indicated that the extraction efficiency increased as a function of time throughout the course of the run. Insofar as these data were derived from the first bench-scale run using a pesticide mixture the results were deemed to be highly promising. This was particularly true in light of the fact that below optimum conditions were chosen with a view towards providing a baseline from which to "fine tune" operational variables.

Subsequent to this initial run, it was decided for reasons of personnel safety and commerical viability to conduct all future runs using hexane as the extraction solvent rather than isopropyl ether. Following the previously described isopropyl ether runs three hexane

Table 10

SEXOP PROCESS RUN NO. 1 SYNTHETIC DDT MIXTURE*

Sample I.D.	Retention Time	Peak Areas	Raffinate[1] Concentration (%)	Extraction[2] Efficiency (%)
Starting Material	8.91	42,310		
	11.45	183,200		
	12.45	50,780		
	14.26	438,900		
		715,190	NA	NA
T_0	8.87	30,650		
	11.45	75,740		
	12.43	73,220		
	14.29	41,460		
		221,070	31	69
T_1	8.91	27,340		
	11.47	93,580		
	12.42	236,600		
	14.30	48,260		
		405,780	57	43
T_2	8.88	23,290		
	11.51	91,200		
	12.48	117,500		
	14.38	29,510		
		261,500	37	63
T_3	8.9	--		
	11.50	28,040		
	12.47	114,100		
	14.38	12,650		
		154,790	22	78
T_4	8.9	--		
	11.53	63,270		
	12.50	55,180		
	14.26	--		
		118,450	17	83
T_5	8.9	--		
	11.4	--		
	12.54	9,956		
	14.42	15,210		
		25,166	4	96
T_6	8.71	13,910		
	11.39	75,580		
	12.41	16,430		
	14.23	14,040		
		119,960	17	83

Notes: % Raffinate[1] Concentration $= \frac{\text{Tn}}{\text{Starting Material}} \times 100$; % Extraction[2] Efficiency = 100 - % Raffinate Concentration

*Solvent - Isopropyl Ether

runs were conducted as follows:

1. A blank was run using only hexane and distilled water to act as a background reference frame for the pesticide runs.
2. A run using saturated DDT and a rotary disc column motor speed of 90.
3. A run identical in all respects to No. 2 above except the motor speed was set at 70.

The bench-scale extractor data sheets for each of these three runs are presented in Tables 11, 12, and 13, respectively. Viewing the data sheets for the saturated DDT solution runs, it will be noted that all run variables are held constant with the exception of motor speed. Motor speed was varied for these runs in order to assess the extraction effects associated with differing rotary disc speeds. It should be noted that the number in the "motor speed" column does not refer to rotary disc rpm, but is rather the setting on the motor control box which has a range from 0 to 100 corresponding to rotary speeds of 0 and 1800 rpm, respectively. A setting of 90 represents an speed of approximately 1600 rpm and a setting of 70 represents an rpm speed of approximately 1000.

The "sample" column in the provided run sheets pertains to specific intervals during the run when aliquots were removed for analysis. The "S" pertains to a sample aliquot of the starting material prior to RDC column influx and the "T" values pertain the aliquots taken subsequent to run initiation.

Analytical data for these three runs are provided in Appendix D of this report. A summary of the extraction efficiencies for the two saturated DDT solution runs is presented in Tables 14 and 15. Viewing the two tables it can be seen that excellent extraction efficiencies were attained for both runs.

Table 11

BENCH SCALE EXTRACTOR
DATA SHEET

RUN # 002
DATE 21 Oct 81
DESCRIPTION Blank H_2O

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
T_0	9:30	90	8	2,000	10	850	100	3,890	10:1	1.39
T_1	10:01	90	6	1,925	10	1,160	100	6,990	10:1	1.39
T_2	11:04	90	6	1,850	10	1,790	100	13,290	10:1	1.39
T_3	11:36	90	6	1,800	10	2,110	100	16,490	10:1	1.39

Comments: Hexane is now the system solvent
These 4 samples were extracted together and concentrated into one 4 ml sample.

Table 12

BENCH SCALE EXTRACTOR
DATA SHEET

RUN # 003
DATE 27 Oct 81
DESCRIPTION Syn DDT

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	9:15					860		3,880		
T_0	9:30	90	6	1,800	10	860	100	3,880	10:1	1.39
T_1	10:00	90	6	1,800	10	1,160	100	6,880	10:1	1.39
T_2	10:40	90	7	1,800	10	1,560	100	10,880	10:1	1.39
T_3	11:00	90	7	1,750	10	1,760	100	12,880	10:1	1.39
T_4	11:30	90	7	1,700	10	2,060	100	15,880	10:1	1.39
T_5	12:00	90	7	1,700	10	2,360	100	18,880	10:1	1.39

Comments: Solvent - Hexane

Table 13

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 004
DATE 29 Oct 81
DESCRIPTION Syn DDT

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	From 003									
T_0	9:05	70	7	1,650	10	860	100	3,880	10:1	1.39
T_1	9:39	70	7	1,650	10	1,200	100	7,280	10:1	1.39
T_2	10:00	70	7	1,625	10	1,410	100	9,380	10:1	1.39
T_3	10:31	70	7	1,600	10	1,720	100	12,480	10:1	1.39
T_4	11:00	70	7	1,600	10	2,010	100	15,380	10:1	1.39
T_5	11:30	70	7	1,600	10	2,310	100	18,380	10:1	1.39

Comments: Solvent - Hexane

Table 14

EXTRACTION RUN NO. 3 USING A SATURATED SYNTHETIC DDT SOLUTION AND A MOTOR SPEED SETTING OF 90

Sample I.D.	Retention Time	Peak Areas	Raffinate[a] Concentration (%)	Extraction[b] Efficiency (%)
Starting Material	9.27	17,564,960		
	9.94	6,632,426		
	10.64	992,727		
	11.81	32,021,164		
		57,211,277	NA	NA
T_0	8.69	119,670		
	9.34	111,745		
	11.14	482,293		
		713,708	1.25	98.75
T_1	8.83	5,773		
	9.54	10,782		
	11.31	28,783		
		45,338	0.079	99.92
T_2	No Discernable DDT Peaks		--	99.99...
T_3	11.55	9,777	0.017	99.98
T_4	11.85	10,011	0.017	99.98
T_5	9.36	4,879		
	11.89	16,818		
		21,697	0.038	99.96

Notes:

$$\text{Raffinate}^{a}\ \text{Concentration}(\%) = \frac{T_n}{\text{Starting Material}} \times 100; \quad \%\ \text{Extraction}^{b}\ \text{Efficiency}(\%) = 100 - \%\ \text{Raffinate Concentration}$$

Table 15

EXTRACTION RUN NO. 4 USING A SATURATED SYNTHETIC DDT SOLUTION AND A MOTOR SPEED SETTING OF 70

Sample I.D.	Retention Time	Peak Areas	Raffinate[1] Concentration (%)	Extraction[2] Efficiency (%)
Starting Material	8.94	16,745,764		
	9.61	6,598,309		
	10.28	872,096		
	11.41	30,251,672		
		54,467,841	NA	NA
T_0	9.09	42,426		
	9.76	17,891		
	11.59	152,553		
		212,870	0.391	99.61
T_1	9.17	29,351		
	9.84	21,472		
	11.69	125,247		
		176,070	0.323	99.68
T_2	11.8	10,751	0.020	99.98
T_3	No discernable DDT peaks		--	99.99...
T_4	11.99	8,094	0.015	99.99
T_5	No discernable DDT peaks		--	99.99...

Notes:

$$\text{Raffinate}^{1}\ \text{Concentration}(\%) = \frac{T_n}{\text{Starting Material}} \times 100; \quad \%\ \text{Extraction}^{2}\ \text{Efficiency}(\%) = 100 - \%\ \text{Raffinate Concentration}$$

It should be noted that these extraction efficiencies were calculated only as a function of the peaks for DDT and its isomers. Some non-DDT peaks are evident in trace analysis on the GC scan, however, the analysis of DDT standards, extraction solvent, and an independent blank run, have shown that these other peaks represent contamination artifacts. These contamination artifacts are introduced by various processing components during the extraction and analysis activities and could not be eliminated without incurring the substantial expense of using nanograde extraction solvents and very time consumming bench-scale extraction appartus cleaning procedures. As such these contamination artifacts are not significant in terms of characterizing the efficiency of the bench-scale system with respect to extraction of DDT and its isomers.

In light of the excellent extraction efficiencies attained during the synthetic DDT runs using the hexane solvent, it was decided to proceed to the next phase of the Task 3 activity involving test runs using real world pesticide manufacturer effluent samples. Activities pertaining to this aspect of the research are addressed below.

3.3.3 SEXOP Runs Using Real World Pesticide Effluent Samples

At the initiation of the bench-scale fabrication activity, a parallel effort was underway to acquire pesticide effluent samples from various U.S. manufacturers. This activity, requiring a considerable negotiations effort on behalf of both EPA and S-CUBED personnel, resulted in the acquisition of the following:

- One 55 gallon sample of DDT effluent from Montrose Chemical Corporation in Torrance, CA.
- One 55 gallon sample of 2,4-D effluent from Rhodia, Inc. in Portland, OR.
- One 55 gallon sample of Bromacil effluent from E.I. Du Pont de Nemours in La Porte, TX.

The DDT effluent sample (used for all experimental runs for this study) was acquired by a Montrose Chemical Company plant engineer under the direction of the EPA Project Officer. The mix of products represented by this sample consist of alkaline wastewater generated from (1) the neutralization and water washing of molten DDT, (2) pump drips and leaks, (3) spent caustic solution from fume scrubbers, and (4) small quantities of miscellaneous non-sewerable wastes collected throughout the plant. The plant was operating normally at the time of sample acquisition and sampling was done at the end of the process at the waste collection tank prior to any control technology. The sample provided to S-CUBED by Montrose Chemical Company was representative of the effluent waste sampled.

The 2,4-D and Bromacil samples also consisted of raw wastewater taken prior to any chemical or biological treatment in the production facility. As such, the suspended solids content is high and the number and diversity of organic constituents is extensive. Since DDT appeared to be the most likely initial run candidate due to its high Kp value, this wastewater sample was submitted to the S-CUBED laboratory for detailed compositional analysis by GC/MS.

The Hewlett-Packard 5830A GC and capillary column were used to determine the pesticide concentrations in the wastewater sample. The chromatogram shown in Figure 11 presents the results of this analysis. Concentrations for DDE, DDD and DDT were determined by calculating the GC peak area from a standard compound injection as shown in Figure 12.

A sample calculation for DDT is shown as follows:

$$\text{DDT in ng/l} = \frac{51252}{33692} \times 10 \times 100 \times 2{,}500 = 3.8 \times 10^6$$

DDT in mg/l (ppm) = 3.8

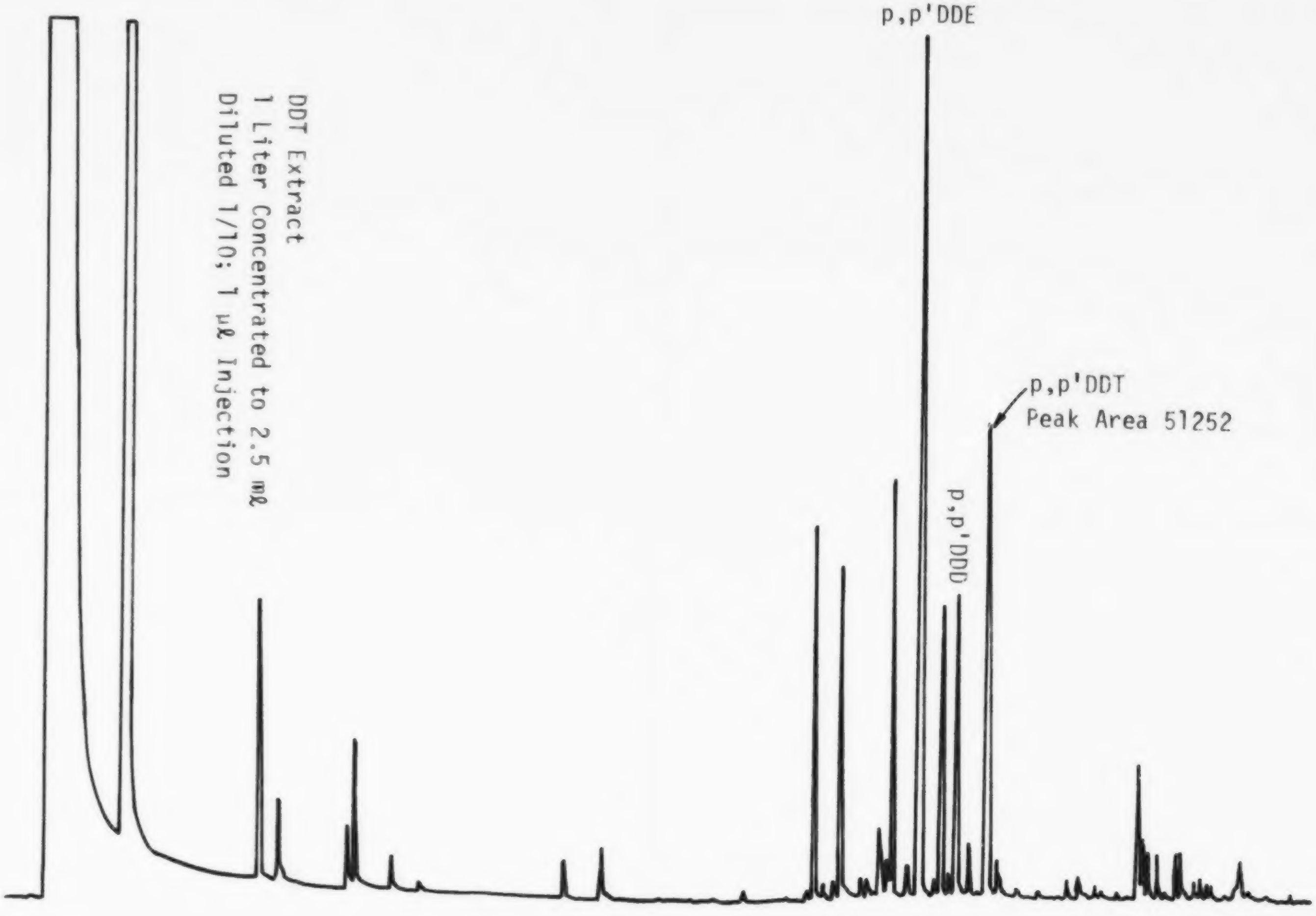


Figure 11 GC Spectrum of DDT Process Water Sample

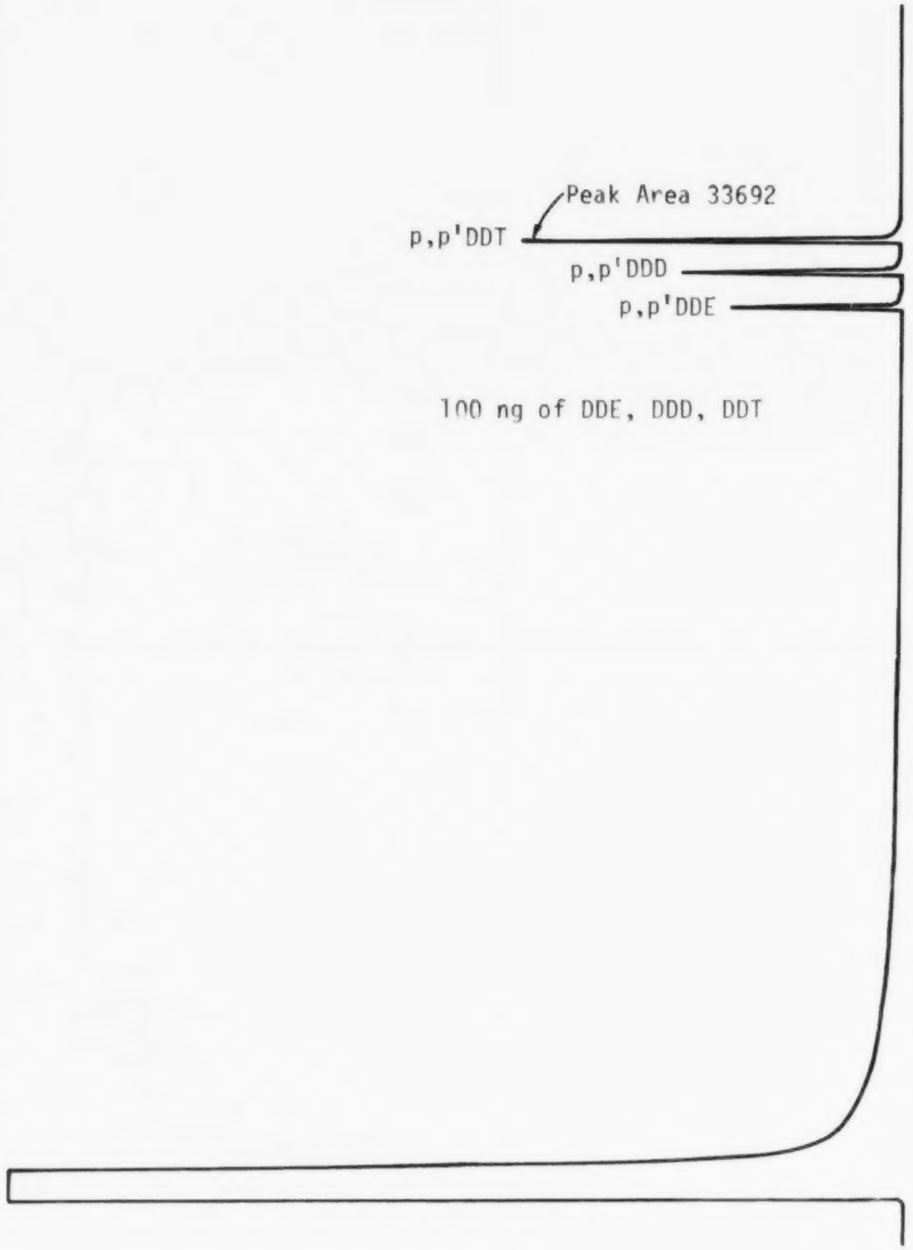


Figure 12 GC Spectrum of Standard Compound of DDT

where:

51252 is the GC peak area for DDT in the sample.

33692 is the GC peak area for a standard compound of DDT.

10 is the dilution factor.

100 is the quantity of standard compound injected (100 ng).

2500 is the normalization factor, since injection volume is 1 μl and total volume of sample is 2.5 ml.

The concentrations for DDE and DDD were calculated as 25.6 ppm and 5.2 ppm, respectively.

GC/MS analysis for the DDT process water sample was conducted using the Finnigan 4021 GC/MS with the INCOS Data System. Three percent OVI column on 60/80 chromosorb was used as column material. The temperature program was set from 50°C to 275°C at a rate of 8°C per minute. The resulting GC/MS data are presented in Appendix E.

The results indicate that chlorinated hydrocarbons (chlorinated benzenes, phenols) are the dominant species in the DDT process water.

There are many isomers of DDT, DDD and DDE compounds (17.26 percent). The amount of chlorinated benzene compounds is 69.4 percent out of total extractable organic chemicals in the DDT process water sample.

Subsequent to the GC/MS analysis, GC analyses were conducted on a regular basis and compared to the original scans in order to assess the stability of the process water sample. These routine checks indicated that subsequent to receipt at S-CUBED, the process sample did not undergo significant alteration.

Following the detailed GC/MS characterization of the DDT process wastewater sample, a series of 4 SEXOP runs were conducted on the DDT effluent. These runs (numbers 006 through 009), were performed with a view toward progressively optimizing the bench-scale design and run parameters in order to obtain the best extraction efficiency possible within the project funding restraints.

The procedure used for the extraction operation involved thorough mixing of the barrel sample for a 24 hour period prior to the run with continued mixing while the run was in progress. The mixed sample contained approximately 20-25% suspended solids, had a pH of 11, and was somewhat viscous due to a high content of solubilized organic and halo-organic compounds. Viewing the Appendix E GC/MS data it can be seen that 52 discrete compounds were identified in this process wastewater sample.

This high concentration of suspended solids and organic material constituted an extremely challenging medium for the bench scale apparatus, in terms of its being representative to a worst-case situation. Nevertheless, the bench-scale system handled the wastewater sample very well with the exception that the high density of suspended solids and organic matter completely precluded the ability to determine sample flow rate using the in-line rotometer. This is reflected by the engineering data sheet for this run presented in Table 16. Although exact flows were not recorded on this data sheet due to the above mentioned problem it was, nevertheless, possible to maintain the appropriate solvent to water ratios by means of maintaining the appropriate levels via observation through the window ports in the RDC column. During the course of future runs this problem was eliminated by means of removing the in-line rotometer and subsequently gauging flow at periodic intervals by direct volumetric measurement using a graduated cylinder, filled over a measured time interval, from a T-fitting plumbed into the process wastewater input line.

Table 16

BENCH SCALE EXTRACTOR
DATA SHEET

RUN # 006
DATE 19 Nov 81
DESCRIPTION DDT Waste

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	3:00	70	6	2,200	10		100	3,880	10:1	1.39
T_0	3:15	70	6	2,100	10	860	100	3,880	10:1	1.39
T_1	3:55	70	6	2,000	10	1,160	100	6,880	10:1	1.39
T_2	4:25	70	6	1,850					10:1	
T_3	4:55	70	6	1,700					10:1	
T_4	5:25	70	6	1,600	10				10:1	
T_5										

Comments: Water flow-in was approximated because of flow meter failure. From T_2 on the solvent-flow was increased to bring interface down and later decreased to bring it up. Viscosity of wastewater presented several problems.
Solvent - Hexane.

Following the bench-scale run, sample aliquots acquired during the course of the run were prepared for analysis using the standard EPA techniques described in Appendix B of this report. Analytical data for this first process sample run were only moderately successful in that many constituents were not significantly reduced during the course of the run. This is illustrated by Figures 13 and 14 which represent chromatograms for run number 006 showing a GC analysis of the starting material compared to an aliquot of the treated water taken during the course of the run.

As a result of these findings two more runs were conducted (numbers 007 and 008) wherein differing run variables were altered in an attempt to improve the efficiency. This manipulation of variables led to the discovery that high turbulence in the lower quadrant of the RDC was contributing to extract solvent entrainment in the treated water effluent.

To compensate for this solvent entrainment problem, a run was conducted wherein motion in the rotary shaft was stopped each time prior to sample acquisition in order to allow greater delineation between phases. This experiment resulted in considerably greater extraction efficiencies as illustrated by the chromatograms for run 009 presented in Figures 15 and 16. As in the case of the previous set of chromatograms, these also show a GC analysis of starting material compared to an aliquot of the treatment water taken during the course of the run. In this case, however, all peaks (except retention time 6.02) are in the mid-to-upper 90th percentile extraction efficiency range. The peak with the 6.02 minute retention time has an extraction efficiency of about 80 percent. The engineering run sheet for this test is presented in Table 17. These latter results are extremely promising, paerticularly considering the highly complex nature of the sample in question. These promising run 009 results clearly pointed in the direction of RDC column design modifications to reduce turbulence in the lowermost extraction zones.

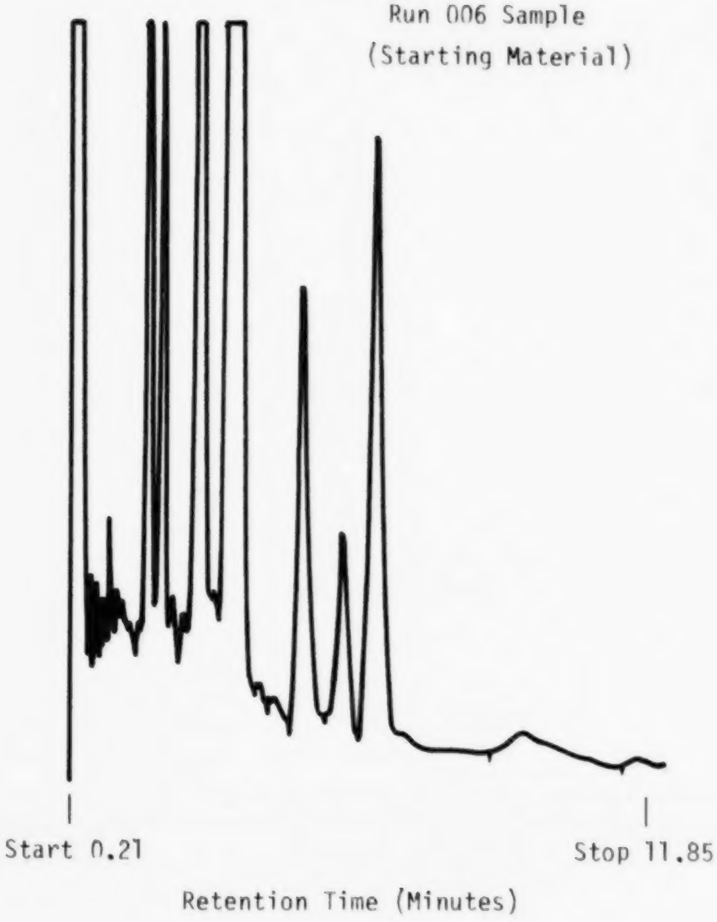


Figure 13 Bench-Scale Run No. 006 - Process DDT Effluent Starting Material

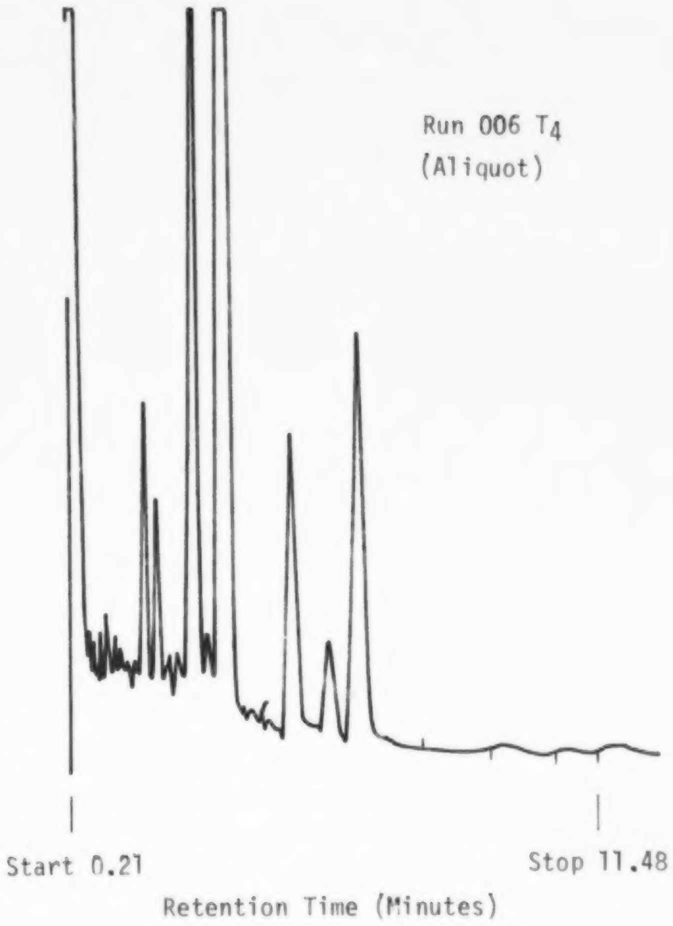


Figure 14 Bench-Scale Run No. 006 - Process DDT Effluent Aliquot No. 4

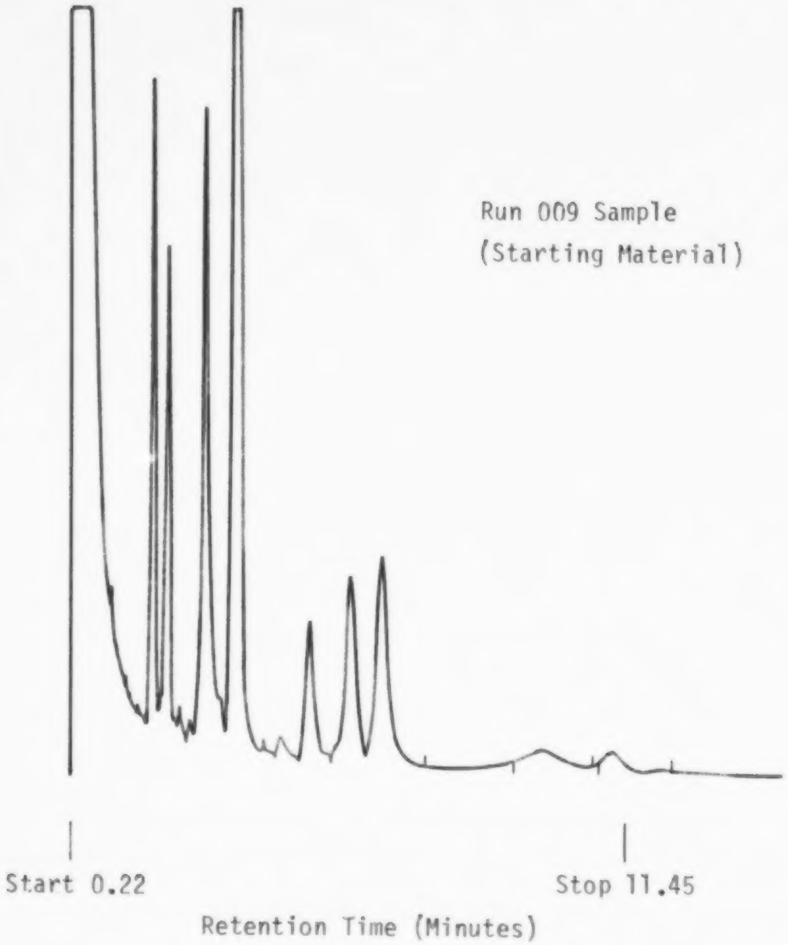


Figure 15 Bench-Scale Run No. 009 - Process DDT Effluent Starting Material

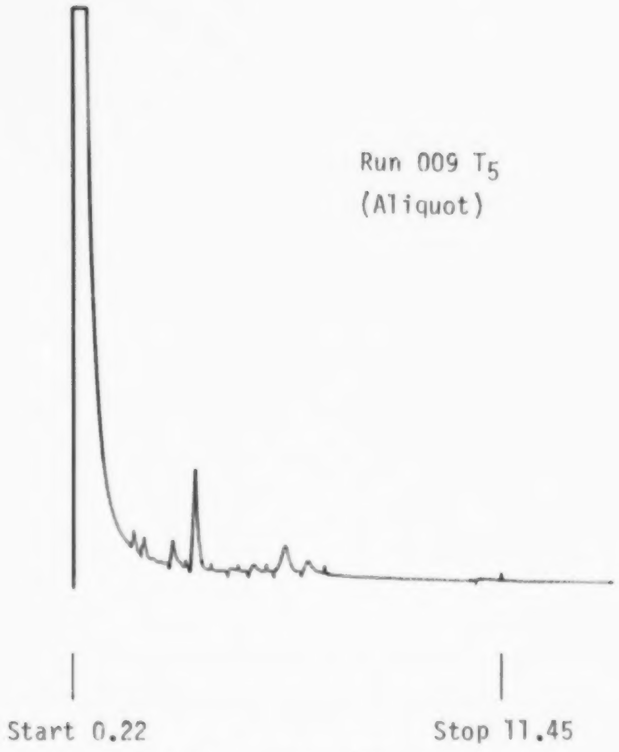


Figure 16 Bench-Scale Run No. 009 - Process DDT Effluent Aliquot No. 5

Table 17

RUN # 009
DATE 12 Jan 82
DESCRIPTION DDT Waste

BENCH SCALE EXTRACTOR DATA SHEET

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	1:00									
T_0	1:45	70	5	1,050	10	1,500	100	3,340	10:1	1.39
T_1	2:15	70	5	1,000	10	1,800	100	6,340	10:1	1.39
T_2	2:45	70	5	950	10	2,100	100	9,340	10:1	1.39
T_3	3:15	70	5	900	10	2,400	100	12,340	10:1	1.39
T_4	3:45	70	5	850	10	2,700	100	15,340	10:1	1.39
T_5	4:15	70	5	800	10	3,000	10	18,340	10:1	1.39

Comments: Motor was turned off for 1 minute before each sample was taken to hopefully avoid hexane contamination.

Table 18

RUN # 010
DATE 15 Jan 82
DESCRIPTION DDT Waste

BENCH SCALE EXTRACTOR
DATA SHEET

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	2:00									
T_0	2:15	70	6	2,200	10	1,500	100	3,340	10:1	1.39
T_1	2:45	70	6	2,200	10	1,300	100	6,340	10:1	1.39
T_2	3:15	70	6	2,175	10	2,100	100	9,340	10:1	1.39
T_3	3:45	70	6	2,150	10	2,400	100	12,340	10:1	1.39
T_4	4:15	70	6	2,125	10	2,700	100	15,340	10:1	1.39
T_5	4:45	70	6	2,100	10	3,000	100	18,340	10:1	1.39

Comments: Solvent - Hexane.

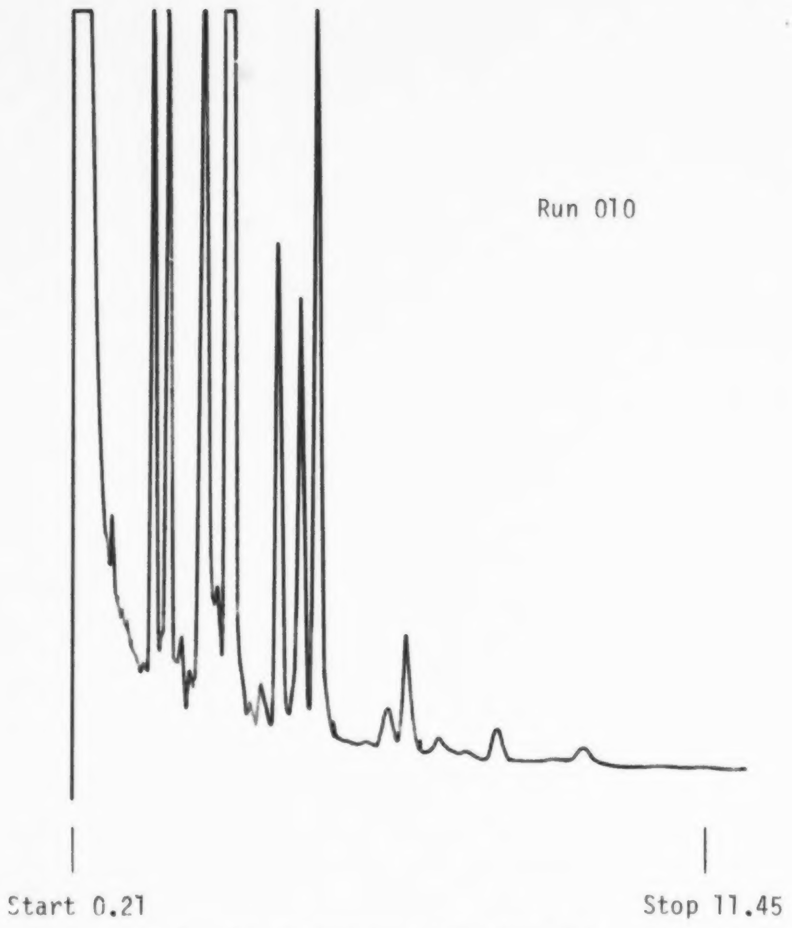
This was accomplished by disassembling the column and removing 5 discs from the RDC shaft base. The RDC extractor was then reassembled and a final bench-scale run (number 010) was performed.

The engineering run sheet for this final experiment is presented as Table 18 and the chromatographic analysis results for the starting material and a run aliquot are presented in Figures 17 and 18 respectively.

Viewing Figures 17 and 18 it can be seen that the engineering design modification was very successful in that the majority of constituents were removed at efficiency levels exceeding 99 percent and there were no removal efficiencies below 90 percent. Furthermore, unlike run number 009, process operation was continuous throughout the experiment resulting in efficiencies superior to any of the previous wastewater sample runs.

Experimental SEXOP runs 006 through 010 resulted in progressively higher extraction efficiencies through the optimization of operational variables and engineering design. Table 19 presents a summary of the bench scale extraction results for runs 006, 009, and 010. Although funding and time constraints necessitated terminating SEXOP research at this point, the results obtained, clearly indicate broad ranging potential for this technology. Based on the success achieved with the DDT process sample to date and considering similar K_p values for a variety of other pesticides, the probability of efficient constituent extraction for other process effluents is high.

Finally, it should be noted that the solvent stripper system performed flawlessly throughout the course of all runs. For a pilot or commercial-scale system this device would be structured much the same except a compressor would be used to reclaim, compress and recycle the nitrogen.



Sample Retention Time (Minutes)

Figure 17 Bench-Scale Run No. 010 - Process DDT Effluent Starting Material

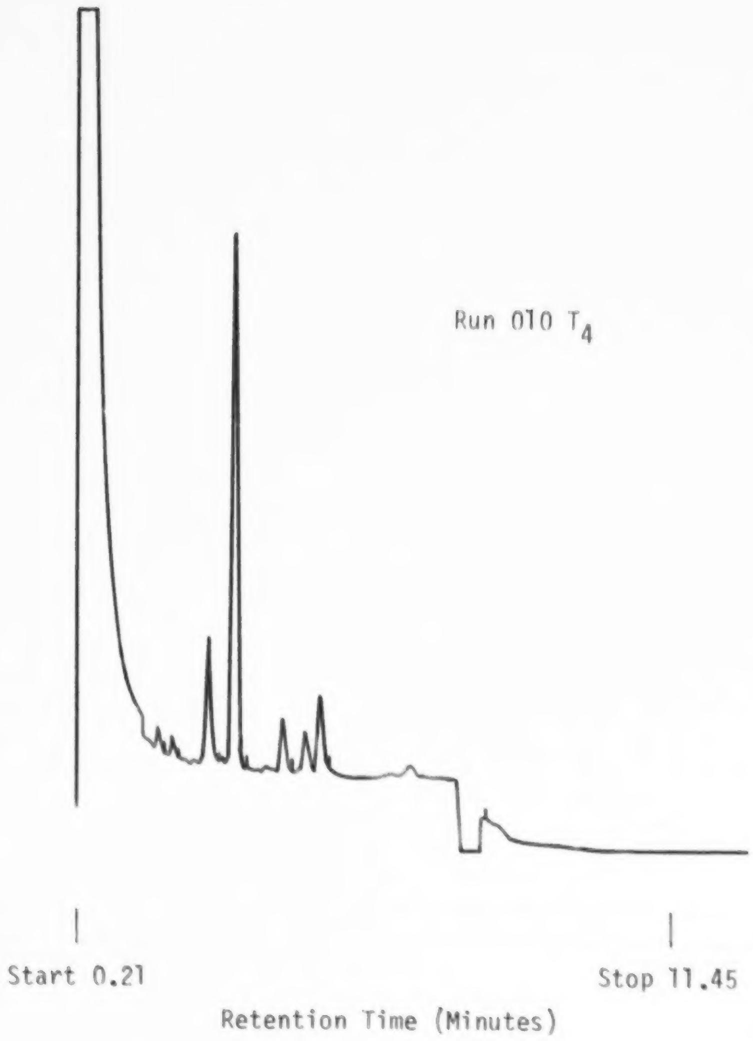


Figure 18 Bench-Scale Run No. 010 DDT Process Effluent Aliquot No. 4

Table 19

BENCH-SCALE EXTRACTION RESULTS FOR RUNS 006, 009, AND 010

Run Number	Extraction Results
006	First bench-scale run on a process effluent sample. Results were only moderately successful in that many constituents were not significantly reduced.
009	Very positive results. All peaks with exception of the 6.02 minute retention time constituent were in the mid-to-upper 90th percentile extraction efficiency range. The peak with the 6.02 minute retention time was extracted at an efficiency of about 80%.
010	Most successful of all runs in that the majority of constituents were removed at efficiency levels exceeding 99 % and there were no removal efficiencies below 90%.

The solvent reclamation condenser was not, at first, successful in reclaiming all solvent. This was due to the lack of sufficient surface area to allow for effective cooling. This problem was solved through use of a water jacketed condenser, which effectively condensed and allowed the recycle of extraction solvent. Insofar as the primary research emphasis for this project was the RDC unit, specific data pertaining to condenser efficiency were not recorded. Estimates based on solvent recovery volumes, however, indicate efficiencies of approximately 95%. Current projections indicate that in a pilot or commercial-scale system, a water cooled or compressor-refrigeration system would satisfactorily perform the solvent reclamation function.

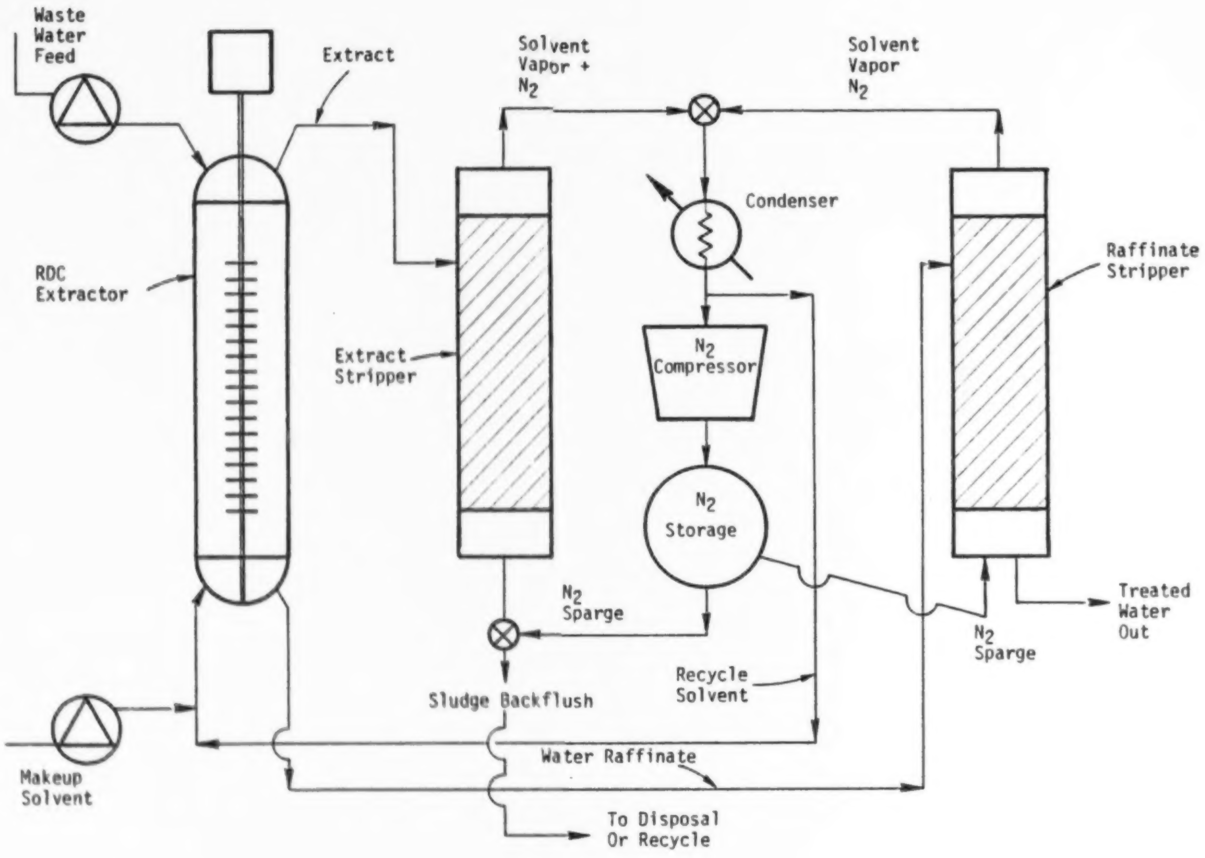
3.4 TASK 4 - ECONOMIC ANALYSIS

The purpose of this task was twofold. First, an effort was made (based on current knowledge) to project an engineering cost estimate for both a small and large commercial-scale Solvent Extraction of Organic Pesticides (SEXOP) Process. Second, an effort was made to compare these cost projections with the more firmly established captial and operational costs associated with carbon adsorption technology.

It must be stressed at the offset, that the provided estimates are intended to represent only general approximations. It is felt, however, that these approximations are sufficiently accurate to support the comparative analysis provided herein.

3.4.1 Cost Models For Commercial-Scale SEXOP Processes

The component parts which would comprise a commercial-scale SEXOP process are integrated schematically in Figure 19. Located beneath this figure is a list of the major captial equipment items which would require an initial expenditure outlay for plant construction. The same components would be required for both a small and large commercial process; only the scale would differ.



CAPITAL EQUIPMENT REQUIRING
INITIAL EXPENDITURE OUTLAY

1) Waste Water Feed Pump
2) Makeup Solvent Feed Pump
3) RDC Shaft Motor
4) RDC Extractor
5) Extract Stripper
6) Solvent Vapor Condensor
7) N_2 Compressor
8) N_2 Storage Vessel
9) Raffinate Stripper

Figure 19 Commercial-Scale SEXOP Process

For the purpose of this discussion a small commercial-scale process would generate a 91,000 gallon/day effluent stream and large commercial-scale process would generate a 910,000 gallon/day effluent stream. These two commercial-scale sizes represent factors of 1,000 and 10,000 times the volume of the bench-scale device fabricated for this study.

An engineering cost estimate has been derived for both of the above commercial-scale model sizes, which presents projections for both capital equipment and operation and maintenance (O&M) parameters. Capital equipment projections (including a bottom line O&M summary) is presented in Table 20. A breakdown of estimated O&M cost projections is presented in Table 21. Sources used to derive the presented costs are cited in the references presented in Section 4 of the bibliography. Projected costs in Tables 15 and 16 represent what is generally called an order-of-magnitude engineering cost estimate with an error range ±30 percent. This type of estimate is satisfactory for the comparative purpose of this project which essentially involves the determination of economic feasibility of solvent extraction technology vis-a-vis carbon adsorption. Estimates of greater accuracy would be possible based on current knowledge, however, these would be extremely time consuming and outside the scope of this project.

All capital costs cited in connection with this study represent "installed costs" which include the initial purchase cost plus all charges incurred while the equipment is being connected into the plant system and made ready for operation.

These installed costs were determined using the Guthrie module approach (4.4). This approach involves the determination of a "Base Cost" for each major piece of processing equipment multiplied by certain "Adjustment Factors" and a "Bare Module Factor". The base cost and each of the accompanying factors is specific to the type of

Table 20

CAPITAL EQUIPMENT REQUIRING INITIAL EXPENDITURE OUTLAY - SOLVENT EXTRACTION

91,000 GPD PLANT		910,000 GPD PLANT	
COMPONENT DESCRIPTION	COST $[1]	COMPONENT DESCRIPTION	COST $[1]
1) WASTE WATER FEED PUMP (NOT EXPLOSION PROOF); 10 HP MOTOR; 3,800 GAL/HR; 60 GAL/MIN.	7,000	1) WASTE WATER FEED PUMP (NOT EXPLOSION PROOF); 100 HP MOTOR; 38,000 GAL/HR; 630 GAL/MIN.	20,000
2) MAKEUP SOLVENT FEED PUMP (EXPLOSION PROOF) 1 HP MOTOR; 380 GAL/HR; 6 GAL/MIN.	5,000	2) MAKEUP SOLVENT FEED PUMP (EXPLOSION PROOF) 10 HP MOTOR; 3,800 GAL/HR; 60 GAL/MIN.	10,000
3) RDC SHAFT MOTOR (EXPLOSION PROOF) 1 HP	600	3) RDC SHAFT MOTOR (EXPLOSION PROOF) 10 HP	1,000
4) RDC EXTRACTION VESSEL (WITH SHAFT & DISCS) 1,300 GAL; 170 FT^3	34,000	4) RDC EXTRACTION VESSEL (WITH SHAFT & DISCS) 13,000 GAL; 1,700 FT^3	205,000
5) EXTRACT STRIPPER - 1,000 GAL; 140 FT^3; INCLUDING STRIPPER TOWER PACKING	23,000	5) EXTRACT STRIPPER - 11,000 GAL; 1,400 FT^3; INCLUDES STRIPPER TOWER PACKING	84,000
6) SOLVENT VAPOR CONDENSER	16,000	6) SOLVENT VAPOR CONDENSER	160,000
7) N_2 COMPRESSOR - 330 FT^3/MIN	23,000	7) N_2 COMPRESSOR - 3,300 FT^3/MIN	110,000
8) N_2 STORAGE VESSEL 50 FT^3	15,000	8) N_2 STORAGE VESSEL 500 FT^3	150,000
9) RAFFINATE STRIPPER - 1,000 GAL 140 FT^3; INCLUDING STRIPPER TOWER PACKING	23,000	9) RAFFINATE STRIPPER - 11.000 GAL 1,400 FT^3; INCLUDES STRIPPER TOWER PACKING	84,000
SUBTOTAL	147,000	SUBTOTAL	824,000
O&M COSTS FOR FIRST YEAR (330 DAYS) OPERATION (SEE TABLE 21)	116,135	O&M COSTS FOR FIRST YEAR (330 DAYS) OPERATION (SEE TABLE 21)	607,734
TOTAL	263,135	TOTAL	1,431,734

[1] ALL ESTIMATES REPRESENT "INSTALLED COSTS".

Table 21

SUMMARY OF FIRST YEAR O&M COST FOR SOLVENT EXTRACTION

SMALL PLANT (91,000 GPD)		LARGE PLANT (910,000 GPD)	
O&M CATEGORY	COST $	O&M CATEGORY	COST $
1) INITIAL SOLVENT CHARGE + MAKEUP	4,000	1) INITIAL SOLVENT CHARGE + MAKEUP	44,000
2) LABOR (ADMINISTRATIVE AND TECHNICAL MIX)	20,000	2) LABOR (ADMINISTRATIVE AND TECHNICAL MIX)	40,000
3) MAINTENANCE	15,000	3) MAINTENANCE	30,000
4) ELECTRICAL (6.3×10^5 KWH)	44,000	4) ELECTRICAL (4.4×10^6 KWH)	308,000
5) DEBT SERVICE AND AMORTIZATION*	30,195	5) DEBT SERVICE AND AMORTIZATION*	169,254
6) REAL ESTATE TAXES AND INSURANCE**	2,940	6) REAL ESTATE TAXES AND INSURANCE**	16,480
TOTAL	116,135		607,734

*AT 10% INTEREST OVER 7 YEARS.

**AT 2% OF THE TOTAL CAPITAL.

equipment under consideration (i.e., each type of equipment has a different set of factors). Following are brief definitions of these key costing relationships.

- Base Cost - Derived from costing graphs consisting of plots over a broad general range for each type of major equipment. For example, base costs for process vessels were derived from a nomograph plotting diameter against height or length against vertical or horizontal fabrication to determine FOB equipment cost in dollars.

- Adjustment Factors - Consider parameters such as material of construction, equipment operating limits, and adjustments to current prices through use of an equipment cost inflation index. These adjustment factors are multiplied by the base cost as follows:

Purchased Equipment $ = [Base Cost (F_m)(F_o) Index]

where: F_m is a material of construction factor and
F_o is an operating limit factor.

The Index used for this study was the Marshall and Swift (M&S) Process Industry Equipment Index.

- Bare Module Factor - Includes all the direct and indirect [illegible] This factor can vary between [illegible] and [illegible] depending on the type of equipment under consideration.

Electrical energy requirements pertinent to the operation and maintenance (O&M) projections are based on $0.07/KWH. Costs for the [illegible] models are based on extrapolation of the bench-scale device which consists of a 4.8 liter (1.267 gallon), rotary disc contactor (RDC) extraction vessel and a 4.17 liter (1.1 gallon) solvent stripper system. Based on bench-scale runs which have produced favorably results on the RDC extraction system, an exchange rate of 3 exchanges per hour was selected as the nominal process flow for the presented models.

Other process component flows, specifications and volumes for both small and large commercial-scale models are presented in the Table 20 capital equipment listing. Generally, these projections are based on actual run criteria for the bench-scale process. The single exception to this is the raffinate stripper which does not have a counterpart in the bench scale system. Design, flow and capacity specifications for this device may be conveniently extrapolated, however, as a function of treated effluent flow from the RDC extractor.

Operation and maintenance (O&M) costs for a commercial-scale SEXOP process are projected as being minimal because the process is predominantly a closed loop system requiring only minor periodic adjustment.

The initial solvent charge consists of sufficient volume to allow for a [illegible] run backlog plus a loss of [illegible] percent of this stock over a 1 year period at a commercial cost for hexane of [illegible] per gallon. Insofar as the solvent is recycled and the raffinate is stripped, solvent losses are expected to be minimal. Also, because the process is designed to operate at ambient temperature, electrical energy requirements are relegated solely to the operation of pumps, compressor and minor utility needs.

Since the SEXOP process is predominantly a closed loop system, labor allocations are primarily associated with routine maintenance activities.

At its current stage of development, the projected O&M costs must necessarily be conjectural. Repeated laboratory runs with the bench-scale system have, however, consistently verified the assumptions used in projecting the costs.

3.4.2 Cost Comparison of the Solvent Extraction Case Costs to Carbon Adsorption

A cost comparison of SEXOP versus carbon adsorption can be made by comparing projected SEXOP costs generated in the previous section with published information on full-scale carbon systems in similar use. A projected large SEXOP plant should be able to process 301 million gallons/year at a cost of $2.02/1,000 gallons.

The component parts which would comprise a typical commercial-scale carbon adsorption process for treatment of pesticide effluent wastes are integrated schematically in Figure 20. Capital equipment and O&M for carbon adsorption cover a broad range and the selection of a specific $/1000 gallons value for comparison to SEXOP may not accurately reflect the real world. Information derived as a result of the literature review effort has shown that, based on total annual cost, carbon adsorption may require from $1.15 to $230.00 per thousand gallons of effluent processed. The most common value cited is around $7.00/1000 gallons. Based on the overall number of citations, in the literature studied, the most realistic range lies between $1.00 to $10.00 per thousand gallons of effluent treated. There are a number of reasons for the discrepancies in the literature for capital equipment and O&M costs for carbon adsorption. Some process variables which play an important role in the wide range of carbon adsorption effluent treatment costs include:

- Concentration of pollutants in the stream being treated.
- Size of the facility ($/1000 gallons treated tend to decrease as the size of the facility increases).
- Whether the carbon is disposed of or regenerated and if regenerated, whether this is done on site or at a central location.
- Location of the facility.
- Effluent purity objective.

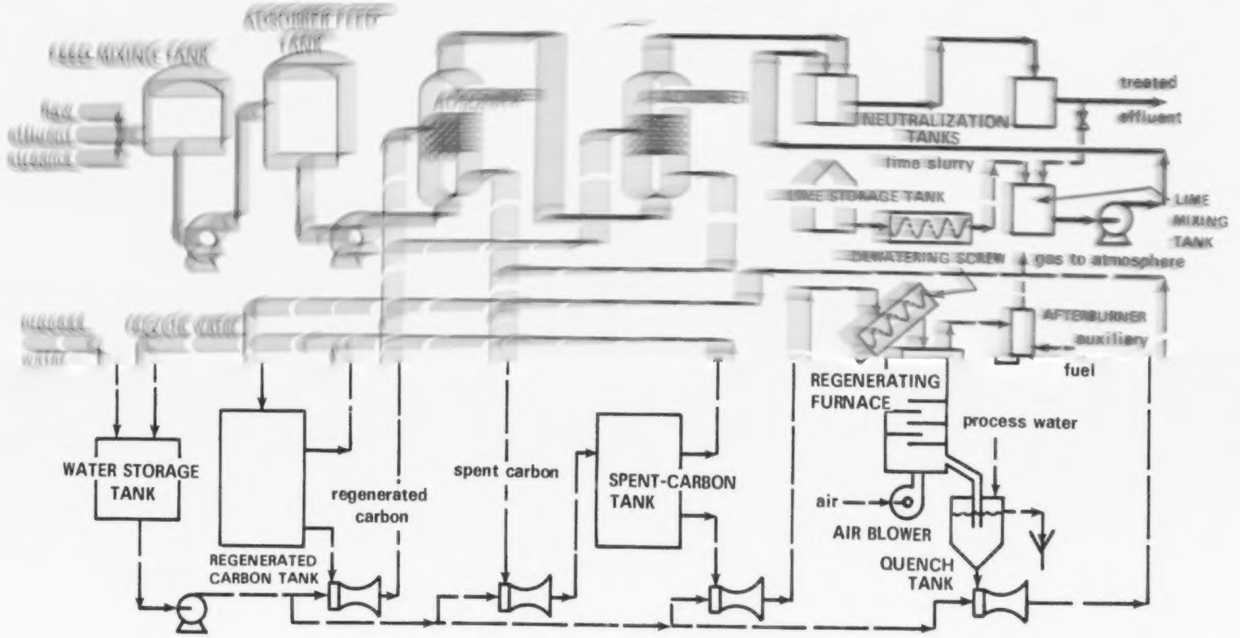


Figure 20 Carbon Adsorption/Filtration Plant For Treating Pesticidal Wastes*

*P.N. Cheremisinoff and F. Ellerbiesch. "Carbon Adsorption Handbook", Ann Arbor Science, An Arbor, MI 1980.

It should be noted, however, that even when the above variables are accounted for, a disparity in processing costs is still frequently evident. For comparative purposes Tables 22-A and 22-B present a list of 14 toxic or refractory industrial wastewater treatment granular carbon installations and their attendant annual processing cost, in terms of $/1000 gallons of effluent treated. The tables were taken from reference 4.2, Chapter 5, entitled, "The Use of Activated Carbon for the Treatment of Pesticides and Pesticidal Wastes". This chapter was written by D. L. Becker and S. C. Wilson of the Industrial Environmental Research Laboratory at Cincinnati, Ohio. Table 22-A presents costs associated with installations using central reactivation and Table 22-B presents costs for installations using on-site reactivation. In both tables, letter designations in the column entitled, "plant" are provided in order to maintain anonymity of the producers from which the data were derived.

Viewing Tables 22-A and 22-B it is possible to gain perspective from the following vantage points:

1. Costs associated with central reactivation versus on-site reactivation can be compared.
2. Capital costs for the entire treatment system can be compared for units of broadly differing flow capacities (using the on-site reactivation case).
3. Table 22-A presents annual operating costs in two separate categories so that the costs associated with carbon reactivation can be compared to those for adsorption treatment.

Table 22-A

TOXIC OR REFRACTORY INDUSTRIAL WASTEWATER TREATMENT GRANULAR CARBON INSTALLATIONS (CENTRAL REACTIVATION)

Plant	Flow (million gal/yr)	Toxic or Refractory Contaminants			Total Annual Cost $/1000 Gallons		
		Average	Influent	Effluent Objective	Absorption Treatment[a]	Carbon Reactivation[b]	Total
A[c]	128	Phenolics TOC	10 mg/l 250 mg/l	0.1 mg/l	0.85	0.80	1.65
B[c]		Phenolics TOC	40 mg/l 300 mg/l	0.1 mg/l	4.00	2.10	6.10
C[c]	183	Phenolics TOC	100 mg/l 600 mg/l	0.1 mg/l	0.35	0.80	1.15
D[c]	11	TOC	900 #/day	60 #/day	3.50	3.45	6.95
E[c]	26	TOC	275 mg/l	Specific Toxicity Test	4.35	2.45	6.80
F[c]	84	Color TOC	800 mg/l	Color Removal	1.50	0.25	1.75
G	55	Phenolics TOC	1700 mg/l 3000 mg/l	0.1 mg/l	1.00	2.00	3.00
H	55	TOC	1000 mg/l	Specific Toxicity Tests	2.00	9.00	11.00

[a] Includes capital, maintenance, insurance and utilities.

[b] Includes reactivation capital, transportation, reactivation utilities and makeup carbon.

[c] Filtration treatment also.

Table 22-B

TOXIC OR REFRACTORY INDUSTRIAL WASTEWATER TREATMENT GRANULAR CARBON INSTALLATIONS (ON-SITE REACTIVATION)

Plant	Flow (million gal/yr)	Toxic or Refractory Contaminants		Type of Thermal On-Site Reactivation	Capital Costs[a] ($000)	Direct Operating Costs ($/1000 gal[b])
		Average Influent	Effluent Objective			
A	6	10,000 mg/l TOC	400 mg/l TOC	Mulitple Hearth	350	20
B	180	370 mg/l Phenolics	10 mg/l Phenolics	Mulitple Hearth	1300	2
C	70	300 mlg/l Phenolics	1 mg/l Phenolics	Kiln	450	1
D	50	100 mg/l Phenolics	1 mg/l Phenolics	Multiple Hearth	300	4
E	550	Color	Color Removal	Kiln	---	--
F	1100	Color	Color Removal	Multiple Hearth	---	--

[a] Includes engineering, construction, adsorption system and reactivation equipment.

[b] Direct operating costs. Does not include depreciation or cost of capital invested.

ANNOTATED

BIBLOGRAPHY

FEASIBILITY OF EXTRACTION OF TRACE LEVEL PESTICIDES FROM PROCESS STREAMS

BIBLIOGRAPHY

The Task 1 Literature Review is specifically oriented toward acquiring information in the following four areas:

(1) Those pesticides manufactured in the United States which are the most environmentally significant, either by virtue of toxicity ranking or by virtue of quantitative manufacture and use.

(2) Solvent systems which can effectively be employed in continuous liquid-liquid extraction systems.

(3) Continuous liquid-liquid extraction engineering process designs.

(4) Economic considerations with respect to solvent selection and process design.

Concomitantly, acquired literature was assigned to one or more of the above four categories, as appropriate. The attached bibliography is, therefore, structured according to the following format:

- Subject category
  - Reference in alphabetical order by author
    - Brief bibliographic statement

FEASIBILITY OF EXTRACTION OF TRACE LEVEL PESTICIDES FROM PROCESS STREAMS

BIBLIOGRAPHY

1. Those pesticides manufactured in the United States which are the most environmentally significant, either by virtue of toxicity ranking or by virtue of quantitative manufacture and use.

1.1 Honea, F.I., D. Dunsak, E.W. Lawless, L.J. Shannon, and D. Wallace. Pesticide Industry. EPA Contract No. 68-02-1324, U. S. Environmental Protection Agency. Research Triangle Park, North Carolina, 1975, Midwest Research Institute, Kansas City, Missouri. 225 pp.

An examination of the pesticide manufacturing industry presenting process flow diagrams and information concerning the characteristics of individual pesticides. Some National manufacturing statistics are also presented.

1.2 Kelso, G.L., R.R. Wilkinson, J.R. Malone Jr., and T.L. Ferguson. Development of Information on Pesticides Manufacturing for Source Assessment. EPA-600/2-78-100, U. S. EPA, Research Triangle Park, NC. 416 pp.

The report addresses the selection of relevant factors to gain perspective of the pollution potential from pesticides manufacturing and formulating operations and leads to the evolvement and defense of decision criteria for assessing the need for development of emissions control technology ...

2. Optimum solvent systems which can effectively be employed in continuous liquid-liquid extraction systems.

2.1 Ahling, B. and S. Jensen. Reversed Liquid-Liquid Partition in Determination of Polychlorinated Biphenyl (PCB) and Chlorinated Pesticides in Water. Anal. Chem., 42(13):1483-1486, 1970.

New method for extraction is described - water is passed through a filter containing a mixture of n-undecane and Carbowax 4000 monosterate on Chromosorb W and the absorbed pesticides are eluted with ether...gas chromatographic system with ECD, the sensitivity is 10 ng/m^3 of lindane of 200 liters. Other pesticides recovered at 50 - 100 percent.

2.2 Ave, W. A., M.M. Daniewski, Jurgen Muller, and J. P. Laba. High-Speed, High-Purity Extraction Apparatus. Anal. Chem., 49(9):1465-1466, 1977.

Apparatus is described and instruction on use is supplied. No data - no actual results. Reference to "hexanes used in pesticide residue analysis...

2.3 Berck, B. Microdetermination of DDT in River Water and Suspended Solids. Anal. Chem., 25(8):1253-1256, 1953.

DDT was determined in concentrations as low as 0.003 ppm. Detailed procedures include means of increasing accuracy when solids absorb pesticide.

2.4 Beroza, M. and M.C. Bowman. Identification of Pesticides at Nanogram Levels by Extraction p-Values. Anal. Chem., 37(2):291-292, 1965.

Partition coefficients are calculated for 16 pesticides between five solvent systems excluding H_2O. Technique and reliability are discussed.

2.5 Beroza, M. and M.C. Bowman. Apparatus and Procedures for Rapid Extraction and Identification of Pesticides by Single and Multiple Distribution in Binary Solvent Systems. Anal. Chem., 38(7): 837-891, 1966.

Apparatus performs many simultaneous extractions rapidly with small volumes - one liquid phase with another. Mathematical equations and graphs relating the distribution of a soluble between equal and unequal phase volumes to its p-value are presented. Twelve pesticides and 4 solvent systems are used.

2.6 Bowman, M.C. and M. Beroza. Device and Method for Determining Extraction p-Values with Unequilibrated Solvents or Unequal Phase Volumes. Anal. Chem., 38(10):1427-1428, 1966.

A modified Erlenmeyer flask is described for more convenient and time efficient analysis of extraction coefficients on seven pesticides. A polar and non-polar solvent system are used in varying phase volumes.

2.7 Briedenbach, A.W., J.J. Lichtenberg, C.F. Henke, D.J. Smith, J.W. Eichelberger, Jr., and H. Stierli. The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters. U. S. Department of Interior, Publishers, 1966, 70 pp.

This report demonstrates sampling, isolating and analyzing procedures used in the past. Contains many references already obtained. Chapter on GC analysis.

2.8 Chiou, C.T., V.H. Freed, D.W. Schmedding, and R.L. Kohnert. Partition Coefficient and Bioaccumulation of Selected Organic Chemicals. Environmental Sci. Tech., 11(5):475- 478, 1977.

An empirical equation is established to relate the experiments n-octanol/water K_p to the aqueous solubilities of a wide variety of chemicals. Such a correlation covering solubilities from 10^{-3} - 10^4 ppm and partition coefficients from 10 - 10^7 allows an assessment of K_p from solubilities with predicted error of less than one order of magnitude.

2.9 Gunther, F.A., ed. Solubilities of 738 Pesticides in H_2O. Residue Reviews, Vol. 20, 200 pp.

The solubilities are listed by chemical and common names of the pesticides. DDT, chlordane, diuron, bromacil, and toxaphene are listed.

2.10 Hansch, C. and T. Fujita. A Method for the Correlation of Biological Activity and Chemical Structure. J. Am. Chem. Soc., 86:1616-1626, 1964.

Part of the paper deals with "Phenyl Ethyl Phosphate Insecticides." Most of paper is on technique. Solvents are not identified.

2.11 Hansch, C., A. Leo and D. Nikaitani. On the Additive-Constitutive Character of Partition Coefficients. J. Org. Chem., 37(20):3090-3092, 1972.

Partition coefficients are compared when methyl groups are added to compounds. Ether, benzene and octanol are solvents used with water.

2.12 Hoffman, W.A. Compact, Variable Volume, Liquid-Liquid Extractor. Anal. Chem., 50(14):2158-2159, 1978.

Continuous liquid-liquid extraction is described for use with rainwater. Methylene chloride is used to extract micrograms of di-2-ethylhexyl phthalate, di-2-ethylhexyl adipate and various chlorohydrocarbons.

2.13 Kahn, L. and C.H. Wayman. Apparatus for Continuous Extraction of Nonpolar Compounds from Water Applied to Determination of Chlorinated Pesticides and Intermediates. Anal. Chem., 36(7): 1340-1343, 1964.

The multichamber arrangement makes it possible to judge the completeness of extraction of a given component from water. Recoveries as high as 100 percent are obtained..." Solvents: ether. Pesticides: DDT, aldrin, endrin, dieldrin, and others.

2.14 Kawahara, F.K., J.W.Eichelberger, B.H. Reid, and H. Stierli. Semiautomatic Extraction of Organic Materials from Water. J. Water Poll. Contr. Fed., 39(4):572-578, 1967.

Equipment to improve time efficiency of hand extractions is described. Recovery efficiencies of pesticides with hexane and mixed solvents are tabulated and gas chromatographic specifications are given.

2.15 Leo, A., C. Hansch and D. Elkins. Partition Coefficients and Their Uses. Chem. Rev., 71(6):525-616, 1971.

Good background on K_D values and equations. One page on methods. Many solvents and solutes. Valuable and long list of partition coefficients.

2.16 Millar, J.D., R.E. Thomas, H.J. Schatlenberg, III. Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Water by Gas Chromatography. Anal. Chem., 53:214-219, 1981.

A study has been made of procedural steps involved in assaying organochlorine pesticides and polychlorinated biphenyls in water. Generally, excellent recoveries were obtained for 25 priority pollutants extracted with dichloromethane and 15 percent dichloromethane in hexane at pHs 2, 7, and 10. The effects of pH, temperature and residual chlorine (2 ppm) on the preservation of these substances for a period of seven days were determined, and best condition for storage are given.

2.17 Neely, W.B., D.R. Branson and G.E. Blau. Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish. Environmental Sci. Tech., 8(13):1113-1115, 1974.

The bioconcentration of several chemicals in trout muscle was found to follow a straight line relationship with partition coefficient...equilibrium concentration of the chemical between a polar and nonpolar solvent (water and n-octanol). Chemicals: hexachlorobenzene, CCl_4, diphenyl ether, and others.

2.18 Rees, G.A.V. and L. Av. Use of XAD-2 Macroreticular Resin for the Recovery of Ambient trace Levels of Pesticides and Industrial Organic Pollutants from Water. Bull. Environm. Cotam. Toxicol., 22:561-566, 1979.

Method using XAD resins for extracting trace levels of organic pollutants from water was successful with five groups of pesticides with 70 to 90 percent success.

2.19 Robbins, W.K. Representation of Extraction Efficiencies. Anal. Chem., 51(11):1860-1861, 1979.

Mathematical aid for efficiency of partition coefficient derived by experiment. Relates conditions to accuracy, regarding number of extracts and volume of solvent.

2.20 Rosen, A.A. and F.M. Middleton. Chlorinated Insecticides in Surface Waters. Anal. Chem., 31(10):1729-1721, 1959.

The processes of carbon filter sampling, adsorption chromatography and infrared spectrophotometry are combined to detect trace levels of eight chlorinated pesticides in water. Method sensitive to identify less than 10 ppb. Method used with aldrin, benzene, endrin and methyoxychlor.

2.21 Schafer, M.L., J.T. Peeler, W.S. Gardner, and J.E. Campbell. Pesticides in Drinking Water, Waters from the Mississippi and Missouri Rivers. Environmental Sci. Tech., 3(12):1261-1269, 1969.

Samples of finished and raw drinking water were assayed for 10 organochlorine pesticides, their metabolites, and related compounds. Included is a statistical evaluation of the one-step extraction method using one-gallon samples to which known amounts of the 14 compounds were added... Solvents: hexane. Pesticides: many

2.22 Veith, G.D. and R.T. Morris. A Rapid Method for Estimating Log P for Organic Chemicals. EPA-600/3-78-049, U. S. Environmental Protection Agency, Duluth, Minnesota, 1978. 16 pp.

> A quick, inexpensive technique based on reverse-phase high pressure liquid chromatography has been developed to estimate the n-octanol/water Kp of organic chemicals. The system consists of a preparative Micro-Pak C-10[12] reverse-phase column eluted with a 15 percent water/85 percent methanol solvent flowing at 2 ml/min at room temperature...

2.23 Voerman, S. Distribution Ratio of Some Chlorinated Hydrocarbon Insecticides between Hexane and Water., Bull. Environm. Contam. Toxicol., 4:64-67, 1969.

> Partition coefficients are generated for six pesticides using separatory flask. Mathematical manipulation allows for water concentration unknown to be calculated from second shake hexane concentration.

2.24 Webb, R.G. Solvent Extraction of Organic Water Pollutants. J. Environm. Anal. Chem., 5(3):239-252, 1977

> Based on experiments with model systems of known organic water pollutants and environmental samples, conclusions are reached concerning the best general solvent for extraction and the most appropriate methods for related manipulations. Solvents: methylene chloride, ether, chloroform, mixtures. Pesticides: None.

2.25 Webb, R.G. Isolating Organic Water Pollutants: XAD Resins, Urethane Forms, Solvent Extraction. EPA-600/4-75-003. Environmental Protection Agency, Athens, Georgia, June 1975. 21 pp.

> "Isolation, separation and concentration into an organic solvent are generally required prior to identification and quantitation of organic pollutants in water by gas chromatography or mass spectrometry. These operations can be simplified or improved by the use of XAD-resins and by changes in solvent extraction procedures. Resin recovery efficiencies were typically 65 to 76 percent for individual compounds; direct chloroform extraction efficiency was 80 percent ...

3. Optimum continuous liquid-liquid extraction engineering process designs.

3.1 Anhoff, M. and B. Josefsson. Simple Apparatus for On-Site Continuous Liquid-Liquid Extraction of Organic Compounds from Natural Waters. Anal. Chem., 46(6):658-663, 1974.

Device is introduced; good methods background. Use of cyclohexane and n-hexane. Pesticde solution mixed with varying amounts of DDT, lindane, aldrin and PCB's.

3.2 Anhoff, M. and B. Josefsson. Apparatus for In-Situ Solvent Extraction of Nonpolar Organic Compounds in Sea and River Water. Anal. Chem., 46(8):1268-1270, 1976.

Device used in water to detect PCB values. Solvents used were hexane and cyclohexane.

3.3 Casamatta, G., D. Bouchez and H. Angelino. Liquid Membrane Separation. Chem. Eng. Sci. 33:145-152, 1977.

Analogy of liquid membrane permeating (LMP) with liquid-liquid extraction has led the authors to study a countercurrent device for LMP separation. A model has been carried out giving the "ideal" performances of a plug flow continuous countercurrent contractor. Results of such a model have been compared with those obtained with two kinds of pilot-scale contractors: a pulsed column and a spray one.

3.4 Earhart, J.P., K.W. Won, C.J. King, and J.M. Prausnitz. Extraction of Chemical Pollutants from Industrial Wastewaters with Volatile Solvents. EPA-600/2-76-220, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1976, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma. 561 pp.

Solvent extraction with volatile solvents was studied as a method for treating wastewaters from petroleum refineries and petrochemical plants. Extraction is most attractive when the loading of organics is high, when substances are present which pose difficulties for biological oxidation, and/or when chemical value of recovered organics is high. Volatile solvents (isobutylene and isobutane) were given particular attention...

3.5 Earhart, J.P., K.W. Won, H.Y. Wong, J.M. Prausnitz, and C.J. King. Recovery of Organic Pollutants Via Solvent Extraction. Chem. Eng. Progr., 73(5):67-73, 1977.

General, but excellent, survey of extraction processes. Report indicates what has been done in several industries and identifies important criteria for solvent selection, economic considerations and design. Good references from this article. Solvents: benzene and many others. Pesticides: none.

3.6 Ferguson, T.L. Pollution Control Technology for Pesticide Formulation and Packagers. EPA-660/2-74/094. Midwest Research Institute, Kansas City, Missouri, January 1975. 154 pp.

Techniques used to dispose of process wastewater include evaporation, landfill disposal, and contract disposal services, including municipal systems. Current pretreatment and treatment techniques for process wastewater discharge are generally considered inadequate to meet increasingly stringent standards. The best practicable wastewater treatment technology appears to be complete evaporation. The best available treatment is a pretreatment-filtration-adsorption process.

3.7 Fleming, R. (ed). Scale-up in Practice. Reinhold Publishing Co., New York, 1958. 134 pp.

This book is comprised of papers from the American Institute of Chemical Engineers Annual Meeting in 1958. It covers scale-up theory, process economics, business economics of plant scale-up, and addresses troubleshooting of some common problems.

3.8 King, C.J. Separation Processes. McGraw Hill, New York, 1971, 360 pp.

This book details chemical and industrial processes for extracting organics from water and removing organics from solvent systems.

3.9 Komasawa, I. and J. Ingham. Effect of System Properties on the Performance of Liquid-Liquid Extraction Columns. Parts I & II, Chem. Eng. Sci., 33:341-347, 479-485, 1977.

Mean drop size, fractional hold-up of dispersal phase, and axial mixing have been determined in a 72-mm diameter packed column, packed with 8-mm glass Raschig rings, using the systems toluene-acetone-water and MIBK-acetic acid-water, in an attempt to assess the effects of the solute transfer processes on column operation...

3.10 Korchinsky, W.J. and S. Azimzadeh-Khatayloo. An improved Stagewise Model of Countercurrent Flow Liquid-Liquid Contactors. Chem. Eng. Sci., 31:871-875, 1976.

An improved stagewise model has been developed to represent more accurately the physical processes occurring in a liquid-liquid extraction column. The influence of drop-size distribution is more realistically represented in this model. The model equations have been solved numerically with a range of parameter values in order to predict the extent of the influence of drop-size distribution on extraction rates...

3.11 Marks, D.R. Chlorinated Hydrocarbon Pesticide Removal from Wastewater. Velsicol Chemical Corp., EPA Demonstration Grant S-803159, 1980, 165 pp.

The method used in this report was XAD-4 Resin Adsorption, chosen over numerous techniques, including solvent extraction. Pesticides: endrin, heptachlor plus H. epoxide, chlordene, hexachloro-norbornadiene.

3.12 Prochazka, J. and V. Jiricny. A Contribution to the Theory of Fractional Liquid Extraction. Chem. Eng. Sci., 31:179-186, 1975.

Analysis is presented of the process of "fractional extraction." A new concept of "critical point" and "limiting lines" has been introduced. Special attention was paid to the conditions for which the system of equations describing the process has a solution. A rapidly converging iterative computational routine has been developed.

3.13 Ricker, N.L. and C.J. King. Solvent Extraction of Wastewater from Acetic-Acid Manufacture. EPA-600/2-80-064. Robert S. Kerr Laboratory, Ada, Oklahoma. 157 pp.

> Solvent extraction was evaluated as a potential treatment. For wastewater samples studied, extraction appeared too costly...

3.14 Scholtens, B.J.R., S. Bruin and B.H. Bijsterbosch. Liquid-Liquid Mass Transfer and its Retardation by Macro-molecular Adsorption. Chem. Eng. Sci., 34:661-670, 1978.

> The transfer of KCI from water to 1-butanol has been measured in a Lewis cell, under laminar flow conditions. This system appears to exhibit no significant interfacial resistance. The effect of spread macromolecules on the mass transfer is shown to be primarily of a hydrodynamic origin. On the basis of the boundary layer theory and the convective diffusion equation, a simple quantitative estimate can be made of the influence of a (partial) rigidification on the transfer process.

3.15 Sobleman, M., K.H. Sweeny and E.D. Calimag. Development of a DDT Manufacturing and Processing Plant Waste Treatment System. EPA-600/2-78-125, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978, 77 pp.

> The report give results of a study both to test the feasibility of detoxification of DDT manufacturing wastes, using solvent extraction, and to develop a practical process. Three different liquid-liquid contacting devices were tested: all provided good extraction of DDT and homologs from the caustic aqueous phase. Major phase separation problems resulted in excessive losses of monochlorobenzene solvent to the aqueous phase. Effort to improve coalescence/phase separation failed...

3.16 Treybal, R.E. Liquid Extraction. McGraw-Hill, New York, 1951. 422 pp.

> This book details the comprehensive aspects of the liquid extraction process. The major topics are liquid equilibria, choice of solvent, mass transfer, calculation, equipment, with many illustrated examples.

3.17 Veith, G.D. and L.M. Kiwus. An Exhaustive Steam-Distillation and Solvent-Extraction Unit for Pesticides and Industrial Chemicals. Bull. Environm. Contam. Toxic, Vol. 7, No. 6, p. 631, 1977.

A modified Nielsen-Kryger steam-distillation apparatus that provides exhaustive distillation of pesticides and industrial chemicals from water sediments and tissue, and the simultaneous extraction of the distillate by a small volume of organic solvent. Solvents: isooctane, toluene. Pesticides: heptachlor, also aroclor, PCB's.

3.18 Werner, A.E. and M. Waldichuk. A Continuous Liquid-Liquid Extractor. Anal. Chem., 34(12):1674-1676, 1962.

Discusses technique used involving polluted sea water. Limited success increases as flow rate decreases. Use of hexane as extracting solvent.

3.19 Water Pollution Control Federation and the American Society of Civil Engineers, a Joint Committee. Wastewater Treatment Plant Design. Lancaster Press, Inc., Lancaster, PA, 1977. 560 pp.

This book presents applicable process theory for water pollution control and addresses design considerations and applications. Subjects are arranged to facilitate use on the basis of a unit process or systems approach. A logical sequence of wastewater treatment plant design is presented.

3.20 Whitehouse, J.D. A Study of the Removal of Pesticides from Water. OWRT A-002-KY(3). Kentucky Water Resources Institute, Lexington, Kentucky, 1967. 175 pp.

The purpose was to investigate some of the properties of pesticides as they exist in water, and to determine the effectiveness of several water treatment processes in the removal of pesticides from water. Among the pesticides investigated were malathion, DDT, aldrin, dieldrin, captan, benzene hexachloride (BHC), 2,4-D, and 2,4,5-T. The water treatment processes include aeration, chemical coagulation, adsorption on activated carbons and clays, and foam separation.

3.21 Wilkinson, R.R., G.L. Kelso, and F.C. Hopkins. State of the Art Report: Pesticide Disposal Research. EPA-600/2-78/183. Midwest Research Institute, Kansas City, Missouri, September 1978. 225 pp.

> This research program was initiated with the overall objective of reviewing published and unpublished information on recent conversion methods. The methods were categorized according to four approaches: incineration; physical/chemical treatment; biological methods; and land disposal. The information was evaluated in terms of the technical data base, economic cost, and environmental impacts...

3.22 Witt, P.A. and M.C. Forbes. By-Product Recovery Via Solvent Extraction. Chem. Eng. Progr., 67(10):90-94, 1971.

> Solvent extraction criteria is discussed with special attention given to recovery and solvent selection. The oil industry and phenol recovery are exemplified in this report.

4. Economic considerations with respect to solvent selection and process design.

4.1 Bauman, H.D. Fundamentals of Cost Engineering in the Chemical Industry. Reinhold Publishing Co., New York, 1964. 364 pp.

> This book covers cost estimation, cost control, manufacturing costs and profitability of ventures. The book provides a practical guide for engineers engaged in the planning, design and construction of chemical process plants. Emphasis is on methods and techniques of cost engineering to yield optimum accuracy when detailed data are limited.

4.2 Cheremisinoff, P.N. AND Ellerbusch, F. (ed). Carbon Adsorption Handbook, Ann Arbor Science Publishers, P.O. Box 1425, Ann Arbor, Michigan, 48106, 1980, 1054p.

> A comprehensive text on the theory of carbon adsorption, its application as a control medium for multimedia effluent, and costs associated with its use as a control technology for a variety of industrial processes including pesticide synthesis.

4.3 Cran, John. Improved Factored Method Gives Better Preliminary Cost Estimate. Chemical Engineering. 88(7):65-79, 1981.

The factored approach to preliminary cost estimating is analyzed statistically and is followed by improvements in the estimating procedure and in the probable accuracy of results. Capital costs, design and past performance of the project's organizers is integrated to help minimize problems and maximize performance.

4.4 Guthrie, K.M. Data and Techniques for Preliminary Capital Cost Estimating. Chemical Engineering. 86(6):80-106, 1969.

An industry standard for cost estimating for a large variety of plant equipment utilizing a module technique for making fast, accurate and consistent cost estimates.

4.5 Hansen, W.G. and Rishel, H.L. Cost Comparisons of Treatment and Disposal Alternatives for Hazardous Wastes. EPA-600/2-80-188. U.S. Environmental Protection Agency, MERL-CI, December 1980.

Unit costs are estimated for 16 treatment and 5 disposal techniques applicable to hazardous wastes from the organic chemicals, inorganic chemicals, electroplating and metal finishing industries.

4.6 Hanson, C. Recent Advances in Liquid-Liquid Extraction. Pergamon Press, Oxford, 1971, 581 pp.

This book covers the chemistry, economics and design aspects of extraction processes. The chemistry is general but the industrial processes are detailed.

4.7 Happell, John. Chemical Process Economics. John Wiley and Sons, Inc., New York, 1958. 290 pp.

This book provides technical information about economic design and operation of chemical process plants. Major points include economic balances, methods for determining profitability, application of treatment to process problems, and implications of economic evaluation and its social implications.

4.8 Happell, J. and D.G. Jordan. Chemical Process Economics. Marcel Dekker, Inc., New York, 1975. 511 pp.

This book provides a working tool to assist chemical engineers in applying technical information to the economic design and operation of process plants. Economic evaluation of process plants, profitability determination, cost estimation for equipment and rates of return are all covered. Economic balances and design are also covered. A useful and informative appendix is also provided.

4.9 Mulligan, J.F. and R.D. Fox. Solvent Extraction. Chemical Engineering, October 18, p. 58, 1976.

Very general overview of advances in the field. Economic aspects are discussed most specifically here. Nothing directly relates to pesticides.

4.10 Ricker, N.L. and C.J. King. Solvent Extraction of Wastewaters from Acetic-Acid Manufacture. EPA-600/2-80-064. U. S. Environmental Protection Agency. Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, April 1980. 168 pp.

Solvent extraction was evaluated as a potential treatment method for wastewaters generated during the manufacture of acetic acid. Possible goals for an extraction process were considered. For the wastewaters studied, extraction appeared to be too expensive unless recovery of a marketable chemical were possible. A cost estimate was prepared for an extraction process.... Direct-fixed-capital, annual operating costs, and return were studied.

4.11 U.S. Environmental Protection Agency. Process Design Manual for Carbon Adsorption - A Technology Transfer Document, October 1973.

Comprehensive examination of design and cost criteria for carbon adsorption effluent treatment technology with values adjustable to current prices through use of the EPA Cost Index.

4.12 Uhl, V.W. A Standard Procedure for Cost Analysis of Pollution Control Operations. Volume II. Appendices. EPA-600/8-79/018b. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1979. 170 pp.

Volume I is a user guide for a standard procedure for the engineering cost analysis of pollution abatement operations and processes. Volume II contains 11 appendices (providing detailed background material) and two comprehensive examples. Appendix subjects are: Capital Investment Estimation, Annual Expense Estimate, the Cash Flow Concept, Discrete and Continuous Interest Factors, Measures of Merit, Cost Indices and Inflation Factors, Rates of Return and Interest Rates, Methods of Reliability and Assessment, and Sensitivity Analysis.

4.13 Viola, J.L., Jr. Estimate Capital Costs Via a New Shortcut Method. Chemical Engineering. 88(7):80-86, 1981.

This time-saving, systematic technique for making a preliminary estimate of a plant's capital cost can be based on the simplist process flowchart. The key factor is a plant's major operating step. The technique consists of determining a function K for the process whose cost is to be estimated. K is then used to estimate the capital cost and then the two are adjusted by a graphic curve (K versus cost).

APPENDIX A

PRE-RUN CHECKOUT PROCEDURES FOR THE SEXOP BENCH-SCALE UNIT

PRE-RUN CHECKOUT PROCEDURES FOR THE SEXOP BENCH-SCALE UNIT

Following fabrication of the SEXOP device, a series of checkout parameters were used to verify operability and performance of the Rotary Disc Contractor (RDC) Column. The principal intent of these checkout runs was to insure smooth functioning of all process components and to allow for the detection of existing or potential malfunctions. This was done in order to avoid the loss of sample (available only in limited quantities) during experimental runs, due to faulty operational or performance characteristics. A typical checkout run involved manipulation of the following parameters:

1. Preparing and charging the water as well as solvent to the feed tanks,
2. Initializing flows in a specific manner that would insure smooth operation and rapid approach to steady state,
3. Allowing sufficient time to reach steady state,
4. Collecting final samples and recording measured flow rates,
5. Terminating flows in a manner that would leave all fuilds in one or another of the tanks with all other equipment empty.

Preparing and charging water and solvent to the feed tanks involved selection of appropriately sized vessels fabricated from materials which would not contaminate either the sample or the solvent. With respect to the sample vessel, preliminary calculations showed that three RDC column exchanges would probably represent the maximum for any experimental run. Since the RDC column has a volume of 4.8 liters (1.267 gallons), three exchanges per run would require a water sample vessel with a volume of approximately 14.4 liters (3.801 gallons). Allowing for a slight safety margin, a sample vessel with a volume of 18.93 liters (5.0 gallons) was selected. The material of construction for this vessel was high density polyethylene. The solvent reservoir consisted of a 3.79 liter (1 gallon) glass container.

Flow initialization required the selection of pumps capable of handling a wide variety of solvent and or contaminated water matrices so as to preclude sample contamination and to allow ease of maintenance. Cole Parmer® peristaltic pumps were chosen for this purpose. These pumps are illustrated in Figure 10 of this report. Flow range for both pumps is 0.0083 to 1.0 liters per minute (0.0022 to 0.2642 gallons per minute).

Flow initialization of both water and solvent was followed by observations to determine the amount of time required in the RDC for the water/solvent mix to achieve steady state. "Steady state" in the RDC column refers to a condition wherein maximum solvent dispersion throughout the water phase has occurred and the water/solvent interface line has achieved stability. This determination is made by visual observation through the glass viewports (refer to Figure 7, of this report).

Following attainment of the steady state condition, water samples were acquired at 30 minute intervals during the course of the checkout run and engineering run parameters (nitrogen stripper gas, solvent, and water flow rates; column exchanges per hour; and rotary disc shaft speed) were recorded on standard run sheets. This was done to simulate a real experimental run so as to insure the establishment of reliable data gathering protocols.

At the conclusion of the checkout run, flows were terminated and final volumes in all reservoirs were recorded as a means of verifying flow data gathered throughout the duration of the run.

APPENDIX B

TASK 2 EXPERIMENTAL PLAN

FEASIBILITY OF EXTRACTION OF TRACE LEVEL PESTICIDES FROM PROCESS STREAMS

TASK 2

EXPERIMENTAL PLAN

The experimental approach used for the Task 2 solubility determinations consists of placing a known amount of a pesticide in water followed by 24 hours of stirring. The solution is then filtered and extracted with an organic solvent. The organic extract which will contain the pesticide that was soluble in water is then analyzed by specific EPA methods. The following methods are employed for the analysis of the pesticides:

	Extraction
Pesticides	Solvent
DDT Chlordane Toxaphene	15 percent methylene chloride in hexane EPA Method 617
2,4-D	Diethyl ether, EPA Method 615
Diuron	Methylene chloride, EPA Method 621
Norflurazon Bromacil Glyphosate	EPA Method not available will follow manufacturer's methods

As a quality control measure, each experiment will be run three times. Step-by-step experimental details are presented in Table B.1 and laboratory data sheets used to record data and calculate values are presented in Tables B.2 through B.4. Important observations pertinent to each experiment are kept in a bound laboratory notebook.

The second set of experiments determine the solubility of the eight pesticides discussed in the above paragraphs in various solvents. The solvents are hexane, pentane, isopropyl ether, butyl chloride, and diethyl ether. The solvents were selected based upon volatility, lack and solubility in water, and polarity. The experiment consists of saturating a pesticide in the organic solvent, separating the solution from the excess residue and determining the soluble smount by gravimetric analsis. The specific details are called out in Table B.5 along with the appropriate data sheets in Tables B.6 and B.7. Again, each experiment is repeated three times as a quality control measure.

Table B.1

SOLUBILITY OF PESTICIDES IN WATER

1. Place 10 mg of pesticide into a 125-ml Erlenmyer flask which contains 100 g of distilled H_2O.
2. Place a Teflon stirring bar in the flask and cover with Aluminum foil.
3. Place flask on top of stirring appartus and stir for 24 hours.
4. At the end of 24 hours, stop stirring and let contents settle for 2 hours.
5. Filter contents of flask.
6. Pour filtrate into a 250-ml separatory funnel.
7. Add 6-ml of solvent to the sample in the separatory funnel and shake funnel vigorously for two minutes.
8. Allow the solvent to separate from the sample, then draw the water into a 200-ml Erlenmeyer flask. Drain the organic layer into a drying column containing 1-2 inches of anhydrous sodium sulfate, and collect it in a 500-ml K-D flask equipped with a 10-ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 6-ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform the third extraction in the same manner.
9. Concentrate the extract in the K-D evaporator on a hot water bath.
10. Analyze by gas chromatography unless a need for cleanup is indicated.

Table B.2

PESTICIDE SOLUBILITY IN WATER
EXTRACTION DATA

DATE________

EXTRACTION DATE________

ANALYST ____________

Pesticide	PRE-EXTRACTION (24-HOUR MIXING)				EXTRACTION		CONCENTRATION	
	Water g	Tare + Pesticide mg	Tare After Transfer mg	Pesticide in Solution	Solvent	Comments	Method	Volume ml
D D T								
Chlordane								
Norflurazon								
Diuron								
Bromocil								
Toxaphene								
2,4-D								
Glyphosate								

Table B.3

PESTICIDE SOLUBILITY IN WATER ANALYSIS DATA

DATE ____________

ANALYST ____________

Pesticide	Method[1]	GC					Solubility ppm
		Sample Dilution	Injection Volume µl	Response	Concentration Detected µg/ml	Pesticide in Sample µg	
D D T							
Chlordane							
Norflurazon							
Diuron							
Bromocil							
Toxaphene							
2,4-D							
Glyphosate							

1 - EPA-EMSL Standard Methods

Table B.4

PESTICIDE SOLUBILITY IN WATER
SUMMARY DATA

DATE ________
EXTRACTION DATE ________
ANALYSIS DATE ________
ANALYST ________

Pesticide	Water ^{A} g	Pesticide in Solution mg	Concentrate Volume µl	GC Injection Volume µl	GC Concentration Detected µg/ml	Pesticide ^{B} in Sample µg	Solubility[1] ppm
D D T							
Chlordane							
Norflurazon							
Diuron							
Bromocil							
Toxaphene							
2,4-D							
Glyphosate							

[1] - Solubility = B/A

Table B.5

SOLUBILITY OF PESTICIDES IN ORGANIC SOLVENTS*

1. Determine mass of glass mixing vial.
2. Place 5 ml of organic solvent in vial, determine total mass.
3. Place enough pesticide into vial to saturate plus extra; determine mass.
4. Place vial into ultrasonic bath for 24 hours to ensure thorough agitation and mixing.
5. After 24 hours, place vial into a centrifuge for two minutes.
6. After centrifuging, transfer solution into a second clean preweighed vial.
7. Pass dry nitrogen gas into first vial with residue at bottom to remove any leftover solvent; once dry, determine mass.
8. Determine mass of second vial (one with just soluble pesticide in it).
9. Subtract Line 7 from Line 3, then subtract that unit from the difference between Lines 1 and 2, this gives the mass of pesticide soluble in solution.
10. Subtract Line 6 from Line 8, then subtract the difference between Lines 1 and 2 from the residue, this should be the same as Line 9.
11. Pass dry nitrogen over the second vial to remove all solvent, therefore, recovering all solubilized pesticides, then determine mass.
12. Subtract mass of second vial (6) from (11) to again determine mass of soluble pesticide.

*Refer to Tables B.6 and B.7.

Table B.6

SOLVENT ______

DATE ______

ANALYST ______

PESTICIDE SOLUBILITY IN SOLVENTS I

Pesticide	$Vial_1$ 1	$Vial_1$ + Solvent 2	$Vial_1$ + Solvent + Pesticide 3	$Vial_2$ 6	$Vial_1$ + Pesticide Residue 7	$Vial_2$ + Solvent + Soluble Pesticide 8	$Vial_2$ + Soluble Pesticide 11
D D T							
Chlordane							
Norflurazon							
Diuron							
Bromocil							
Toxaphene							
2,4-D							
Glyphosate							

Table B.7

SOLVENT ____________

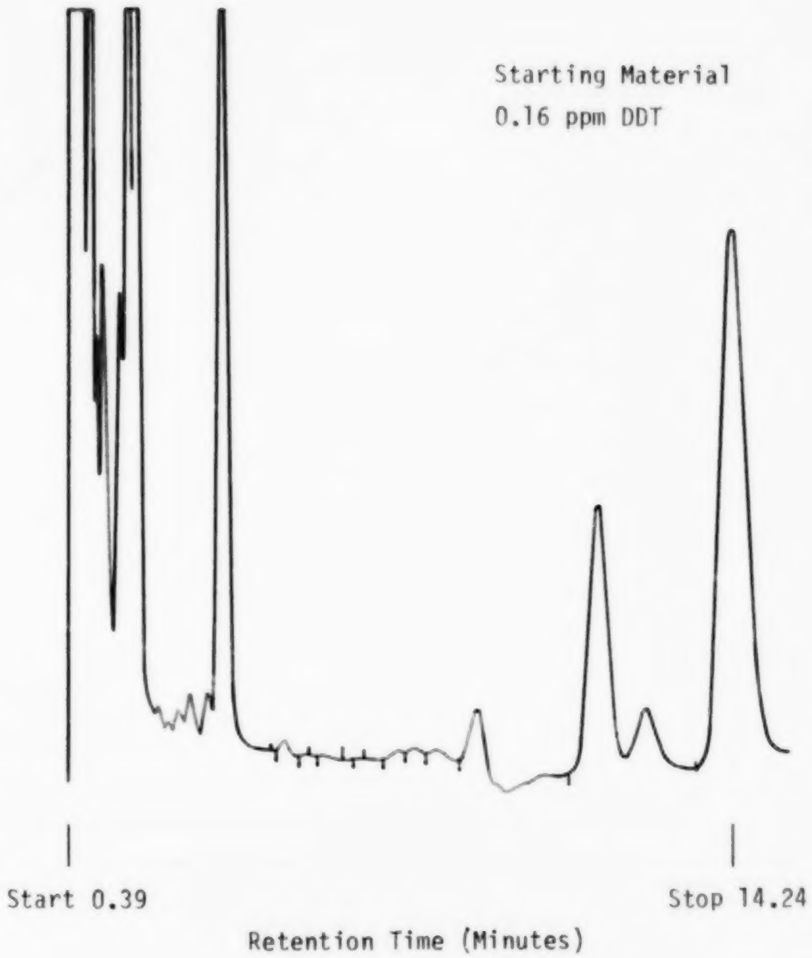
PESTICIDE SOLUBILITY IN SOLVENTS II

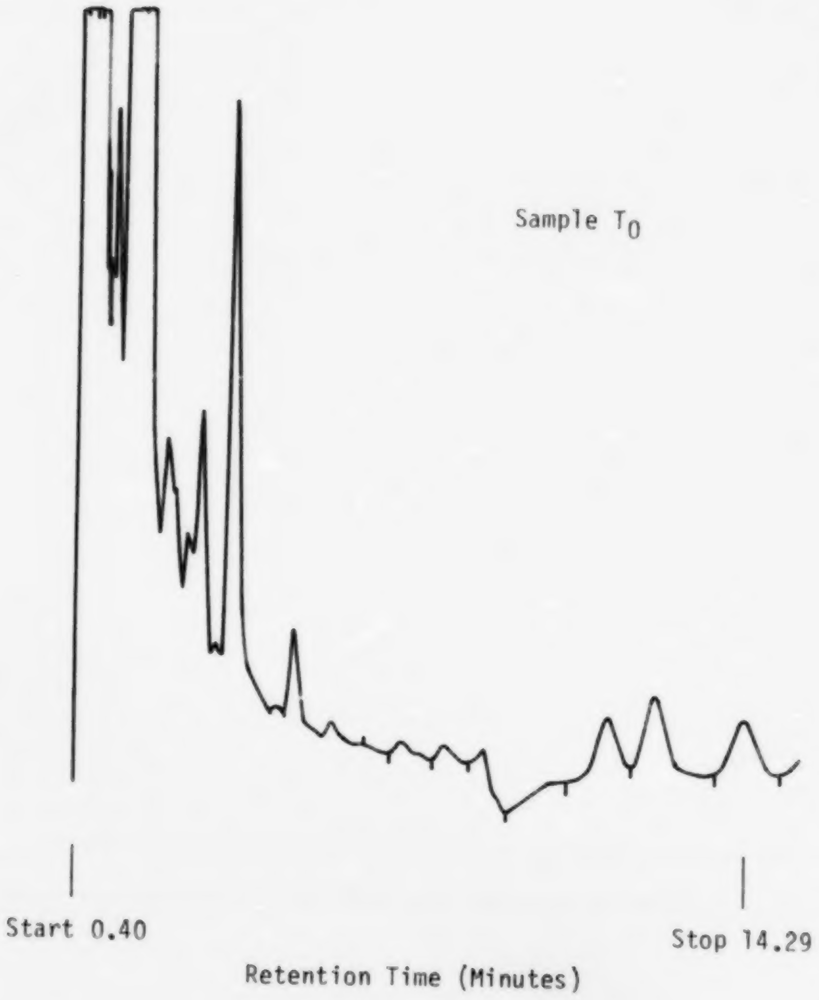
DATE ____________
ANALYST ____________

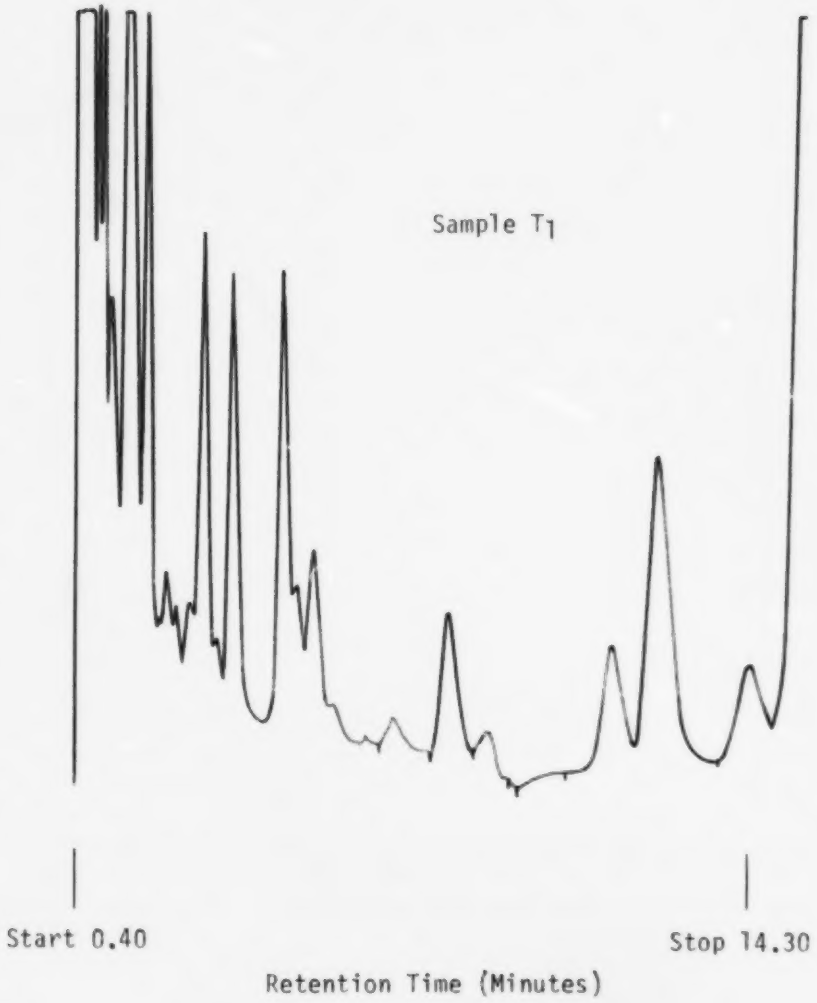
Pesticide	9-A Solvent + Soluble Pesticide (3) - (7)	9-B Soluble Pesticide (9-A) - (2-1)	10-A Solvent + Soluble Pesticide (8) - (6)	10-B Soluble Pesticide (10-A) - (2-1)	12 Soluble Pesticide (11) - (6)
D D T					
Chlordane					
Norflurazon					
Diuron					
Bromocil					
Toxaphene					
2,4-D					
Glyphosate					

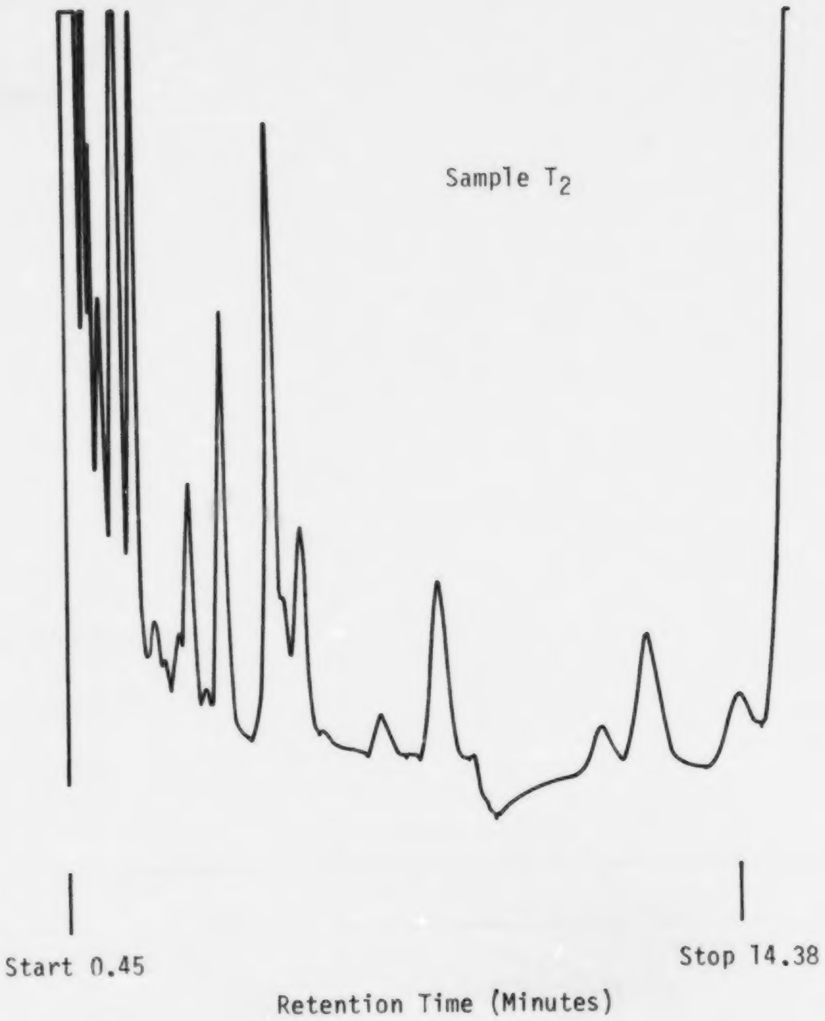
APPENDIX C

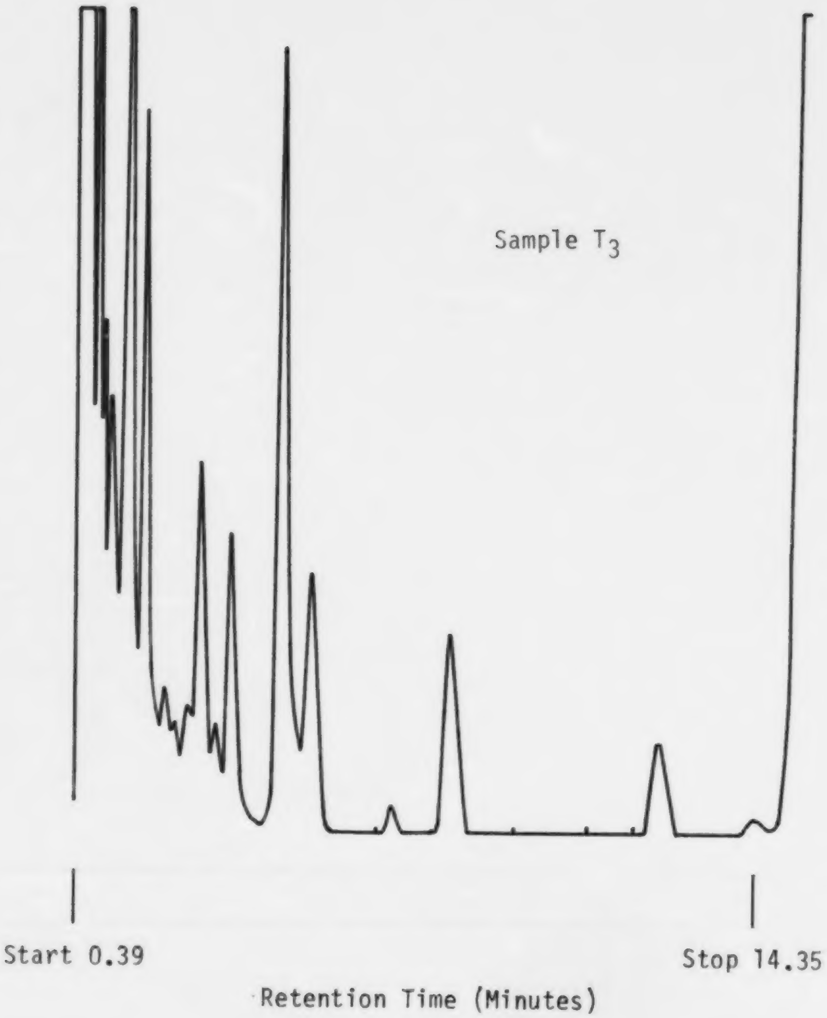
GAS CHROMATOGRAPHIC DATA
FOR
RDC SYSTEM RUN NO. 1
USING
A SYNTHETIC DDT FEED STREAM

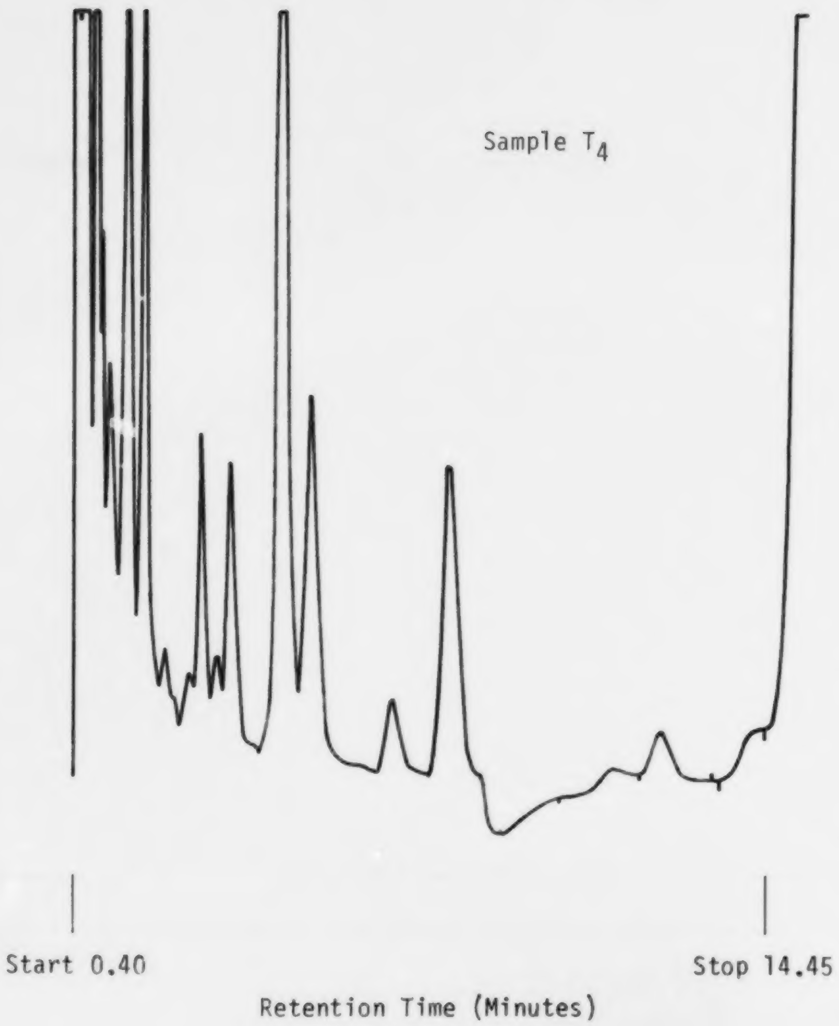

Starting Material
0.16 ppm DDT
Start 0.39
Stop 14.24
Retention Time (Minutes)

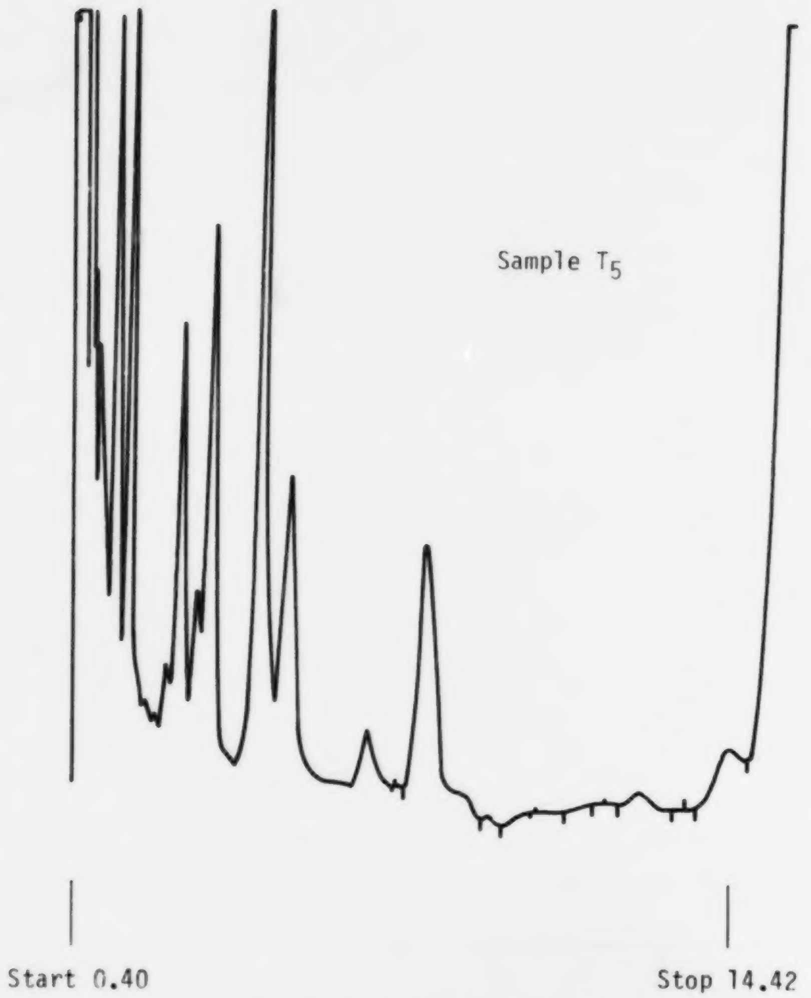

Sample T_0
Start 0.40
Stop 14.29
Retention Time (Minutes)

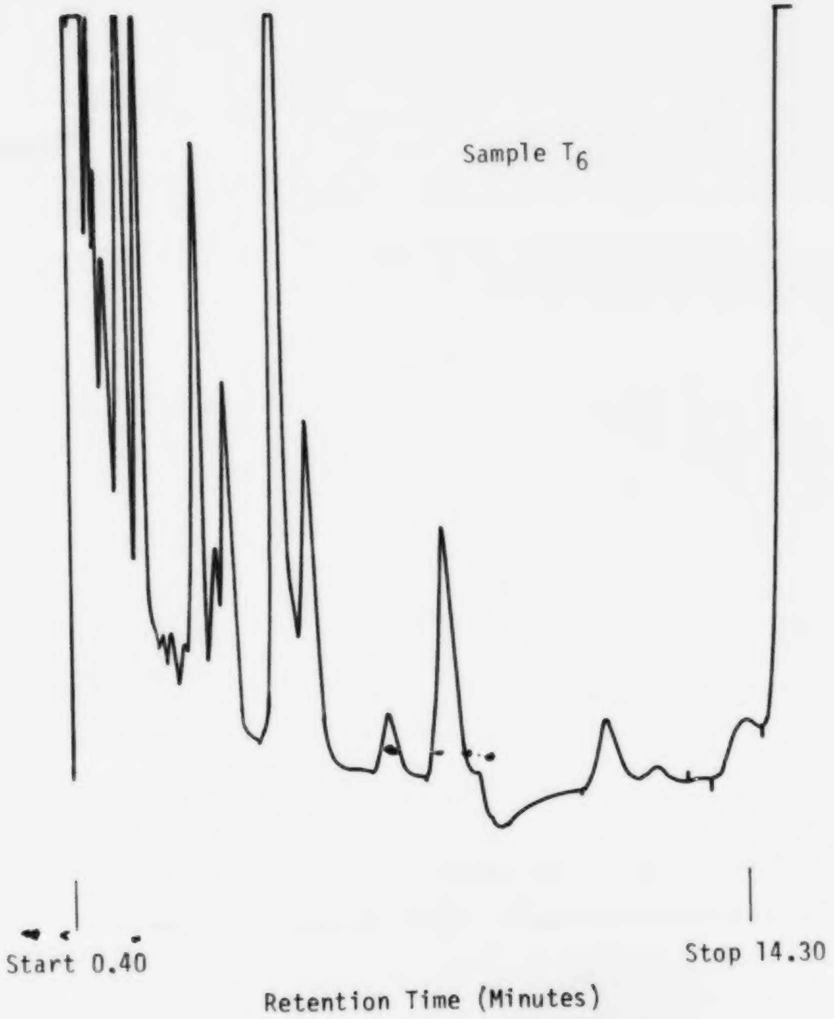

Sample T_1
Start 0.40
Stop 14.30
Retention Time (Minutes)


Sample T_2
Start 0.45
Stop 14.38
Retention Time (Minutes)


Sample T_3
Start 0.39
Stop 14.35
Retention Time (Minutes)

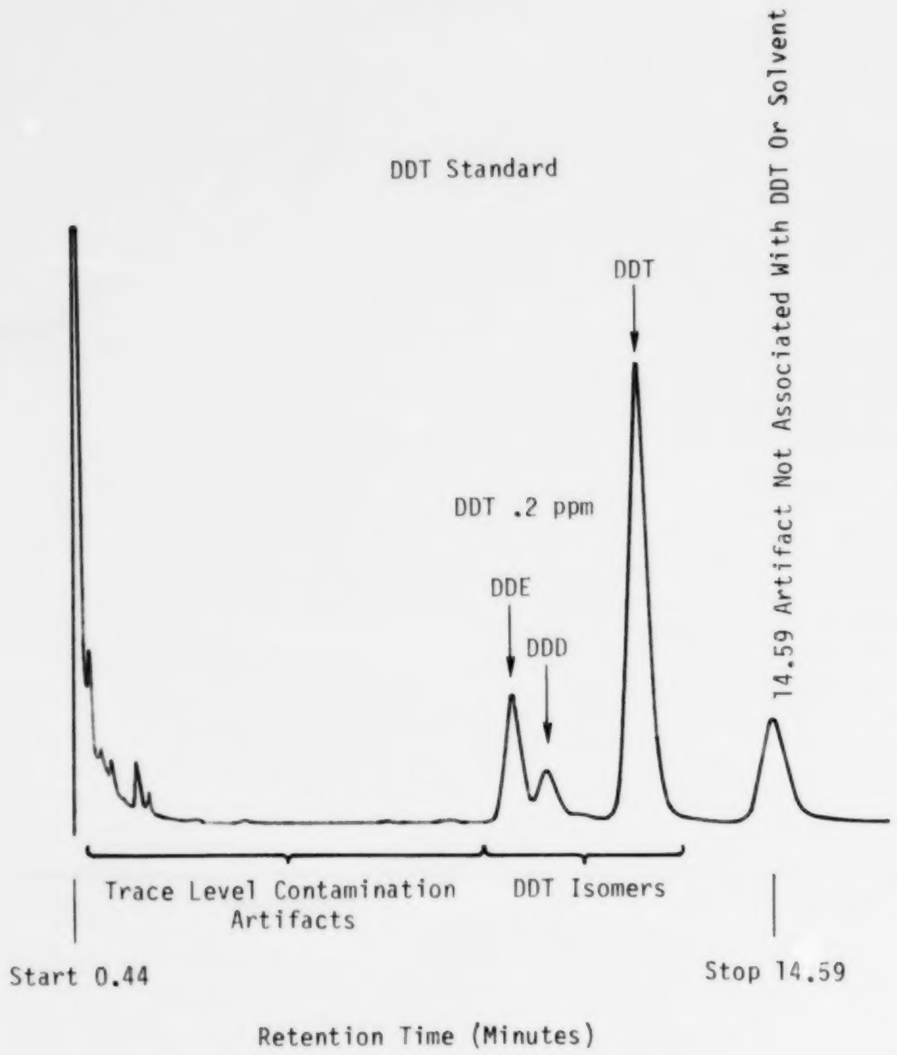

Sample T_4
Start 0.40
Stop 14.45
Retention Time (Minutes)

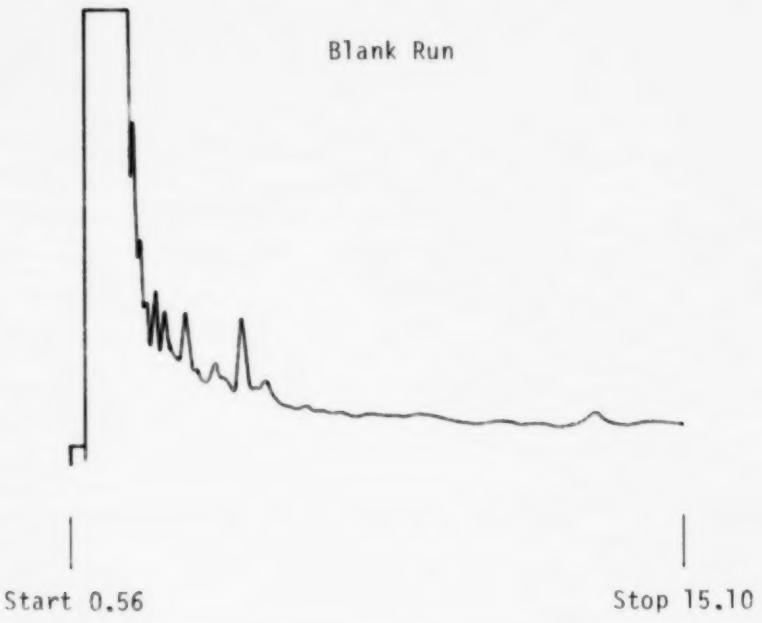

Sample T_5
Start 0.40
Stop 14.42
Retention Time (Minutes)


Sample T_6
Start 0.40
Stop 14.30
Retention Time (Minutes)

APPENDIX D

GAS CHROMATOGRAPHIC DATA
FOR
RDC SYSTEM RUNS 2, 3, and 4
USING
A SYNTHETIC DDT FEED STREAM


DDT Standard
DDT
DDT .2 ppm
DDE
DDD
14.59 Artifact Not Associated With DDT Or Solvent
Trace Level Contamination Artifacts
DDT Isomers
Start 0.44
Stop 14.59
Retention Time (Minutes)

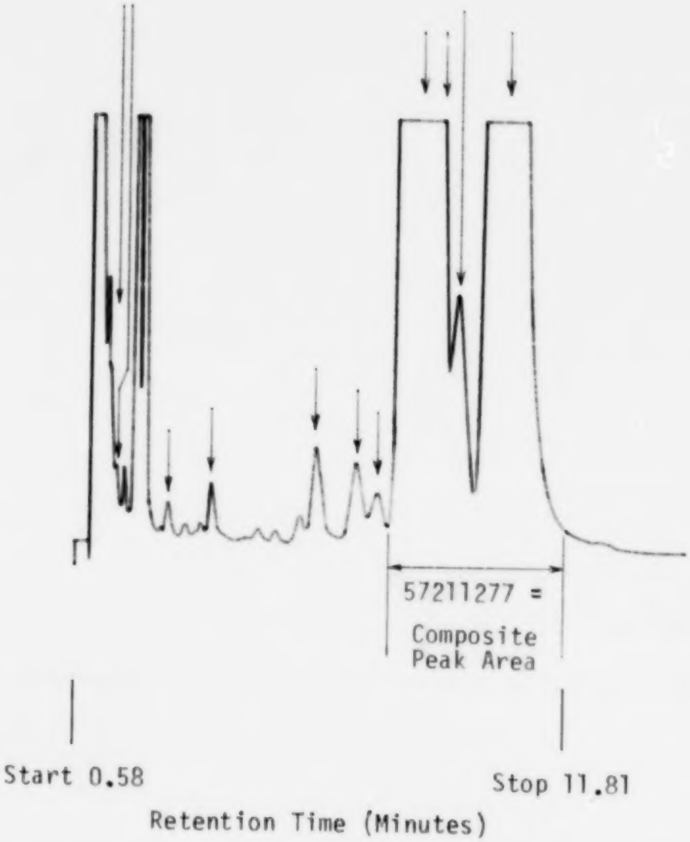


Retention Time (Minutes)

Blank Run Representing A Composite Of Three Aliquots
Taken At ½ Hour Intervals -
Hexane And Distilled H_2O

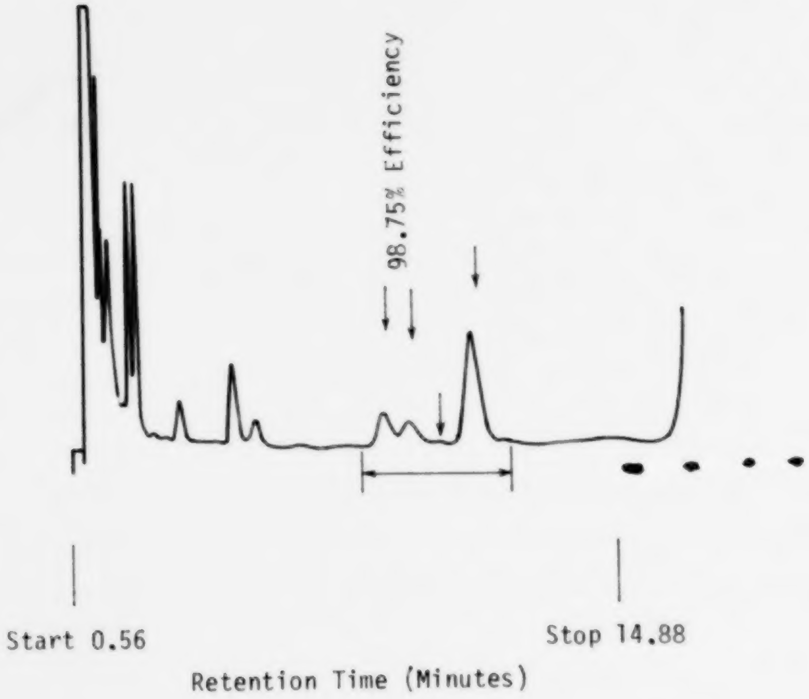
Run 003

Starting Material

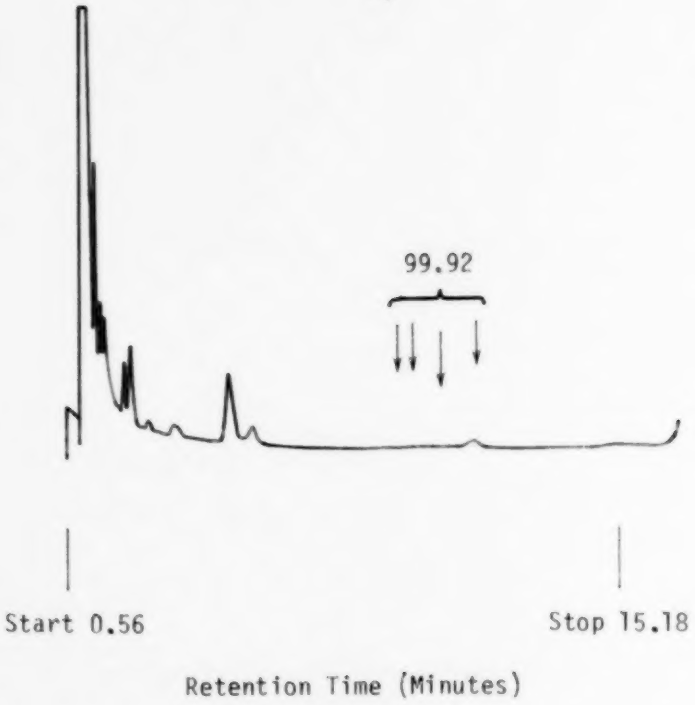


Run 003

T_0

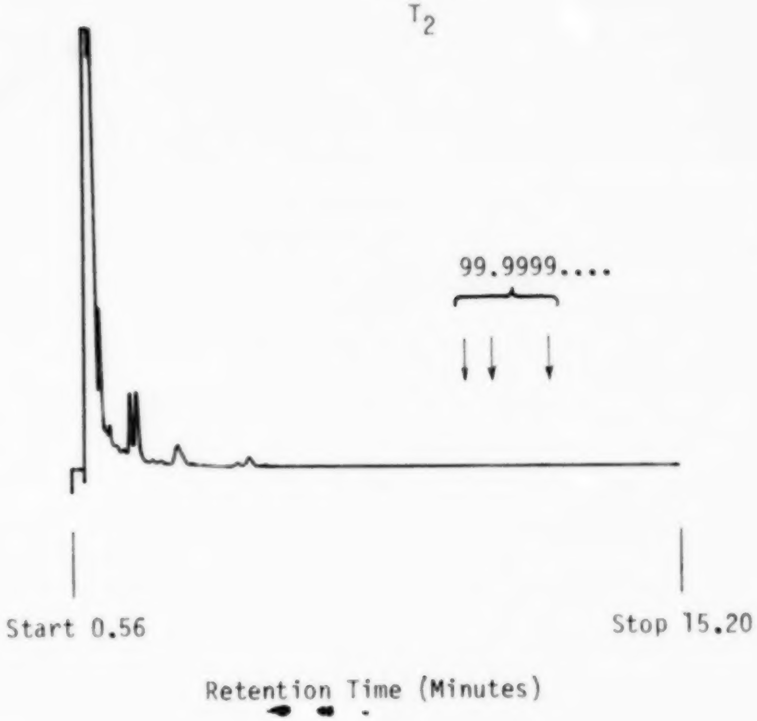

98.75% Efficiency
Start 0.56
Stop 14.88
Retention Time (Minutes)

Run 003
T_1



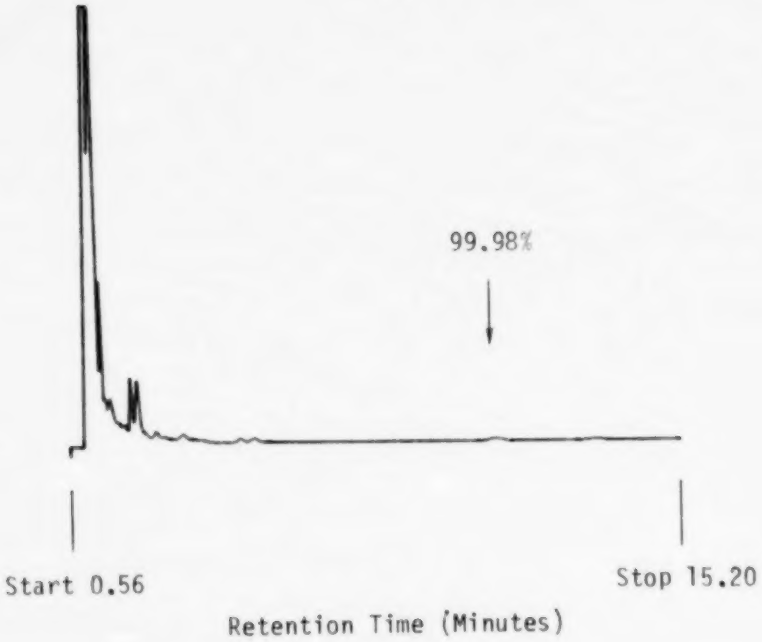
Run 003

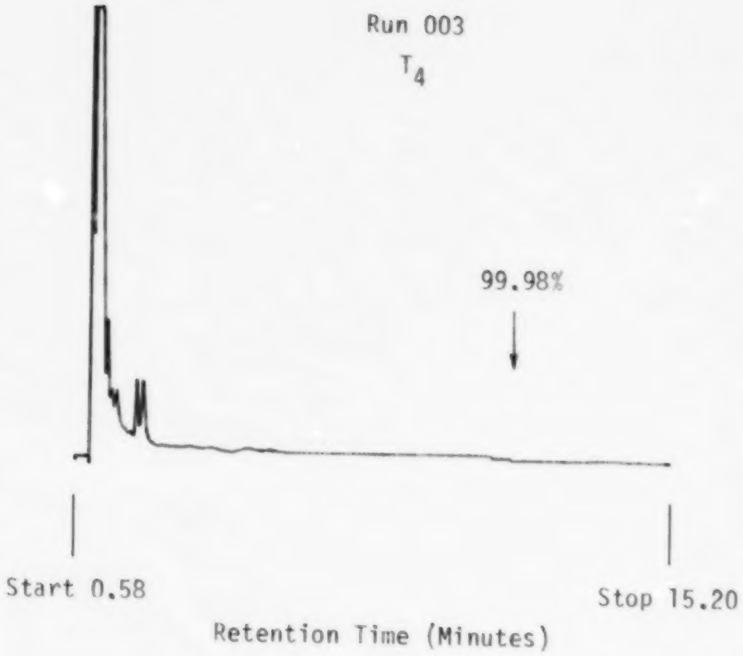
T_2

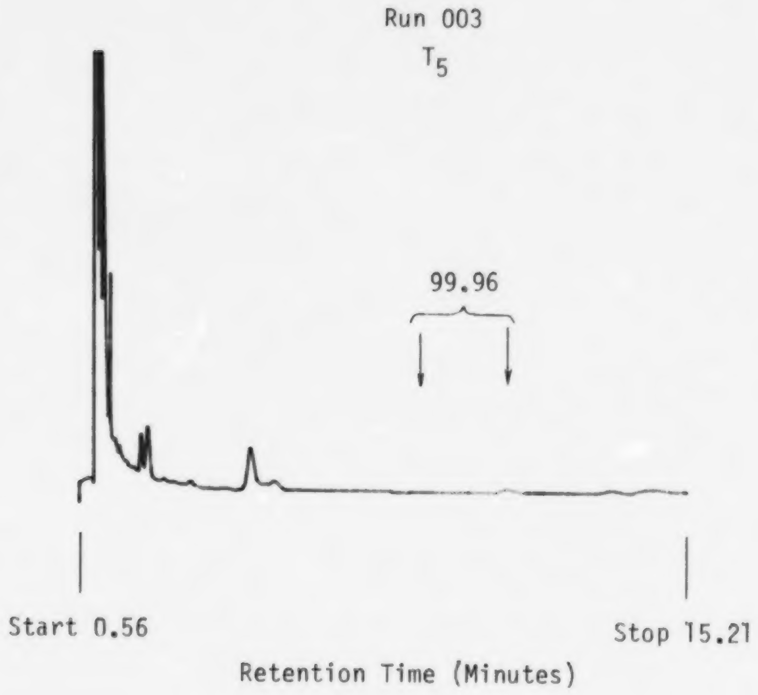


Run 003

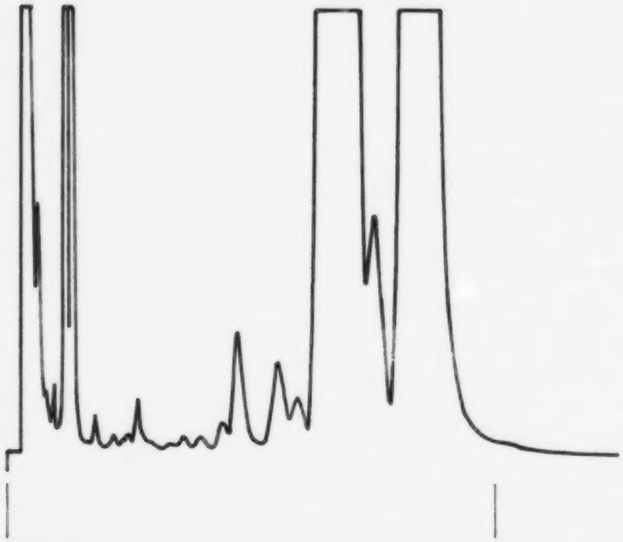
T_3

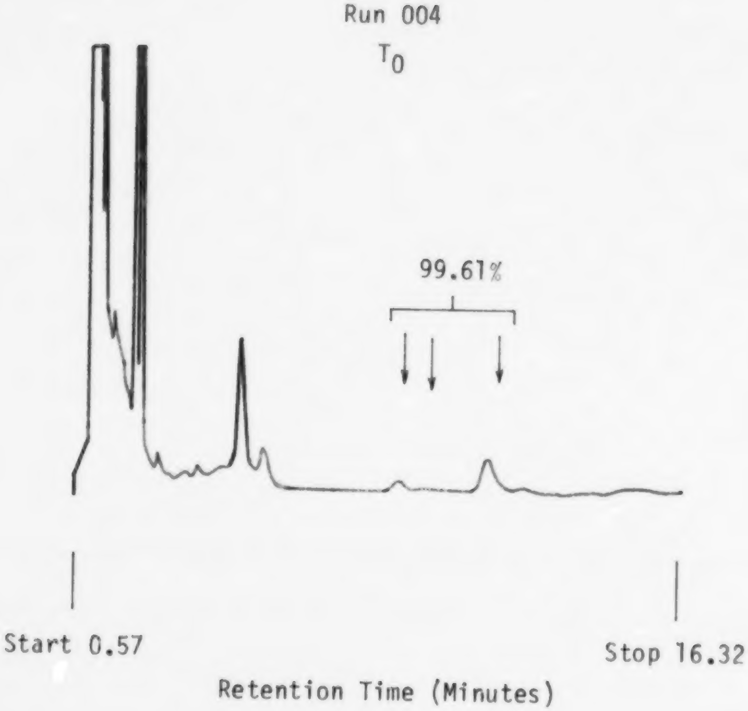


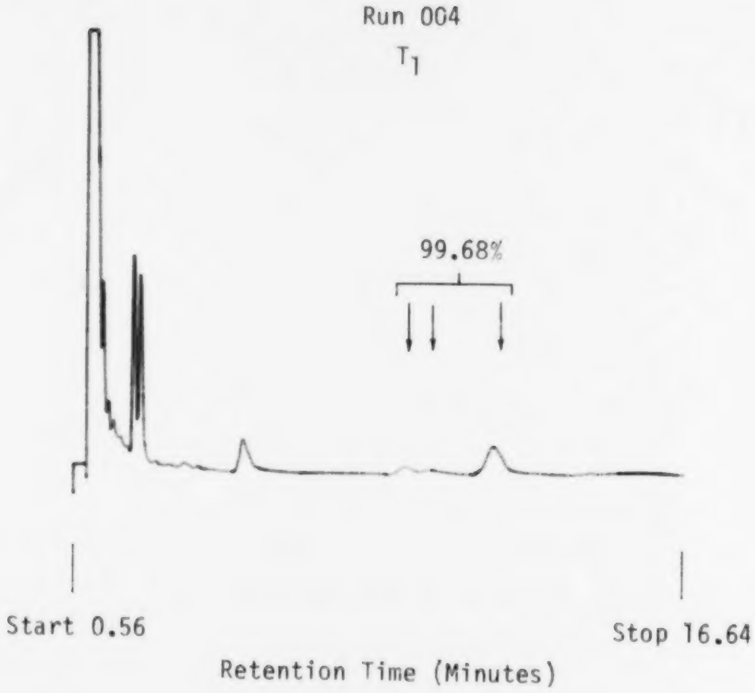

Run 003
T_4
99.98%
Start 0.58
Stop 15.20
Retention Time (Minutes)

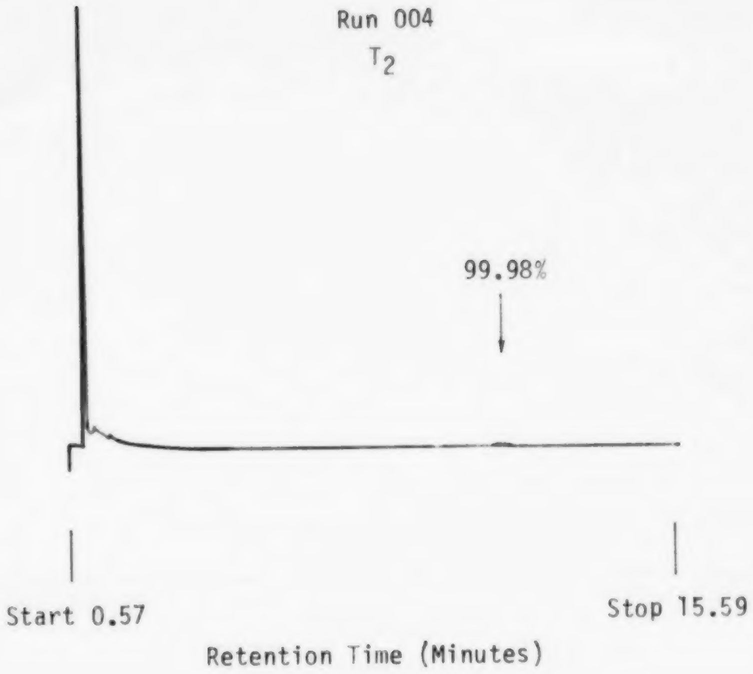

Run 003
T_5
99.96
Start 0.56
Stop 15.21
Retention Time (Minutes)

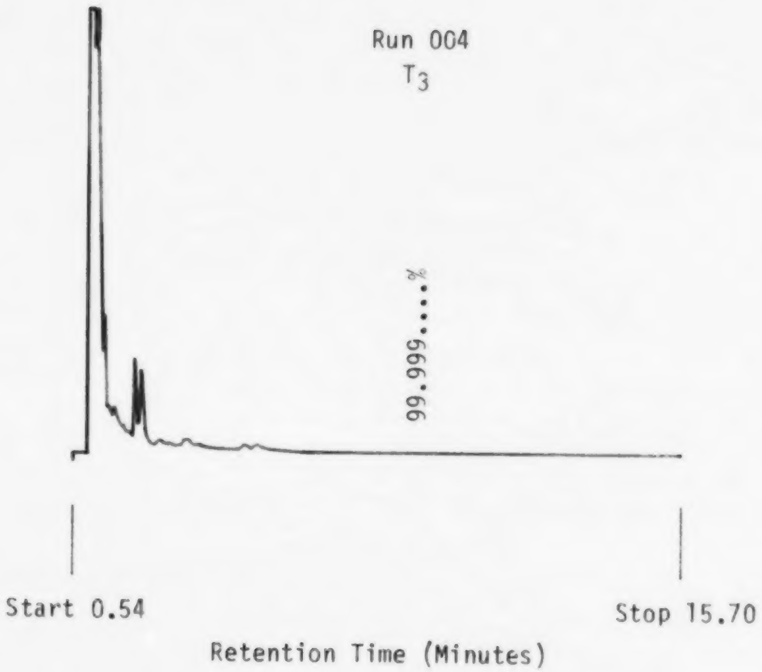
Run 004
Starting Material

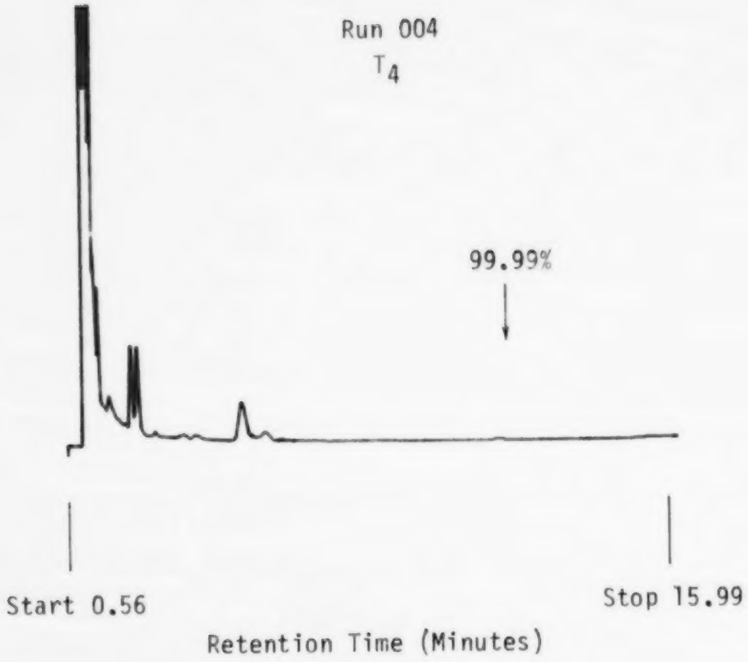



Run 004
T_0
99.61%
Start 0.57
Stop 16.32
Retention Time (Minutes)


Run 004
T_1
99.68%
Start 0.56
Stop 16.64
Retention Time (Minutes)

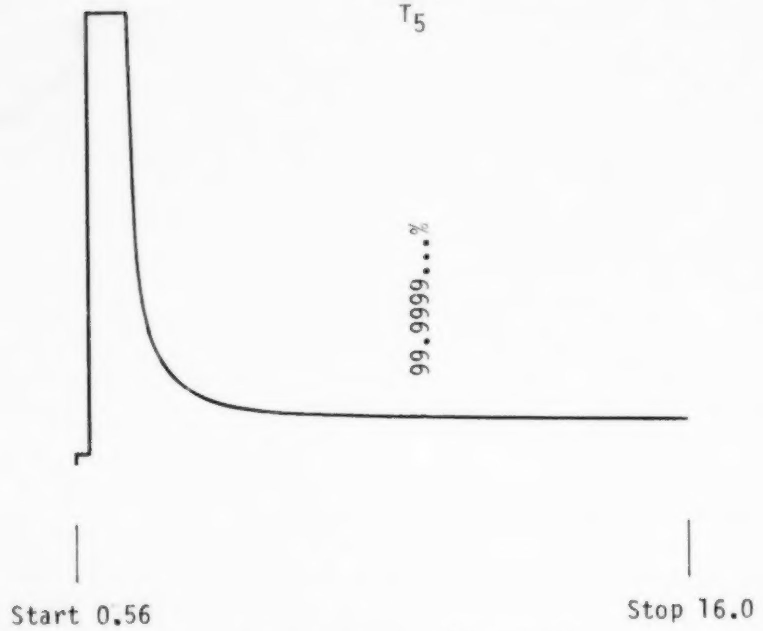

Run 004
T_2
99.98%
Start 0.57
Stop 15.59
Retention Time (Minutes)


Run 004
T_3
99.999....%
Start 0.54
Stop 15.70
Retention Time (Minutes)


Run 004
T_4
99.99%
Start 0.56
Stop 15.99
Retention Time (Minutes)

Run 004

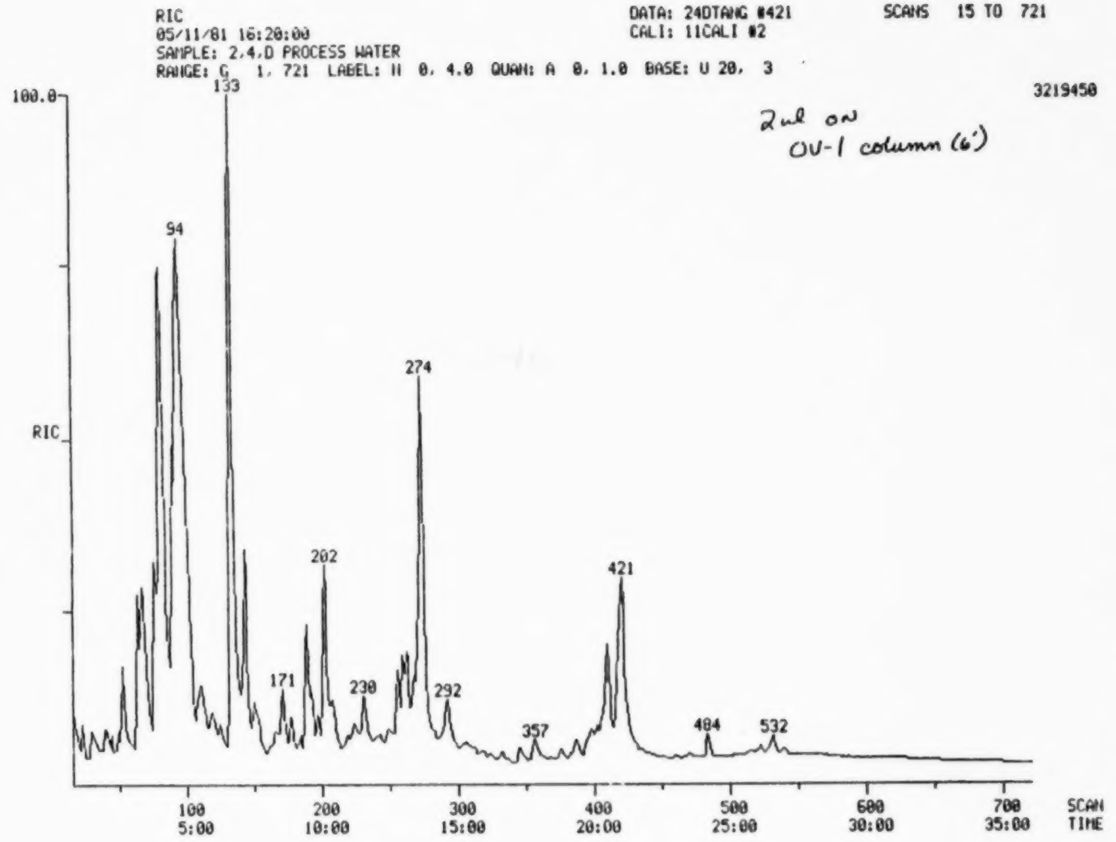
T_5



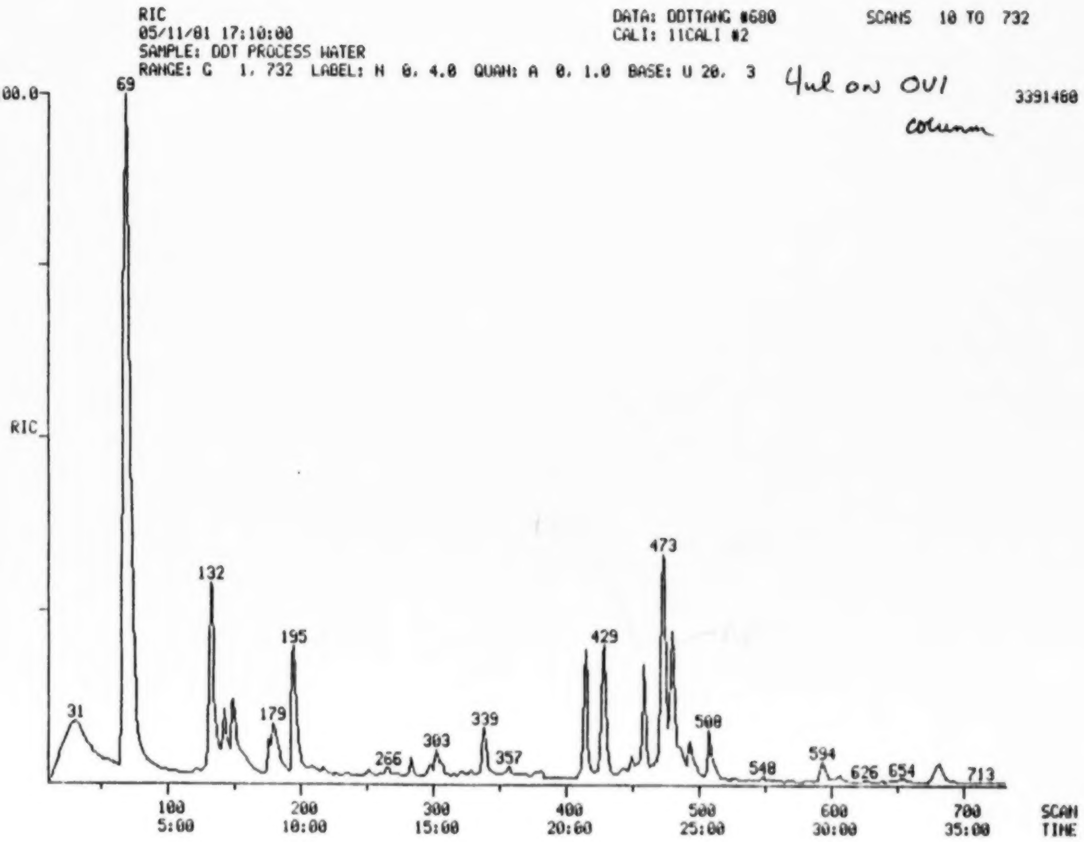
Retention Time (Minutes)

APPENDIX E

GC/MS ANALYSIS DATA
FOR THE
DDT AND 2,4-D PROCESS SAMPLES



GC/MS Spectrum of 2,4-D Process Water Sample



4ul on OV1 column

GC/MS Spectrum of DDT Process Water Sample

```
GUANTITATION REPORT         FILE: OUTLIST

DATA: DDTTANG.TI
05/11/81 17:10:00
SAMPLE: DDT PROCESS WATER
CONDS.:  50(5 MIN)-275 @ 8 DEG/MIN
FORMULA: OV 1 COLUMN         INSTRUMENT: 4021              WEIGHT:      0.000
SUBMITTED BY: J TANG         ANALYST: JW                   ACCT. NO.:

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

 NO  NAME
  1  METHANE,DICHLORO-
  2  METHANE,DICHLORO-
  3  BENZENE,CHLORO-
  4  1-PENTENE,3,4-DIMETHYL-
  5  BENZENE,1,4-DICHLORO-
  6  1-HEPTANOL,6-METHYL-
  7  BENZENE,1,4-DICHLORO-
  8  ISOOCTANOL
  9  PHENOL,2,5-DICHLORO-
 10  PHENOL,2,4-DICHLORO-
 11  PHENOL,4-CHLORO-
 12  BENZENEMETHANOL,2-CHLORO-
 13  BENZENE,DICHLOROMETHOXY-
 14  BENZENEMETHANOL,2-CHLORO-
 15  BENZENE,1,2,3,4-TETRACHLORO-
 16  ISOOCTANOL
 17  ISOOCTANOL
 18  THIAZOLO\5,4-D\PYRIMIDINE,2,5-DICHLORO-
 19  2H-CYCLOPROPA\A\NAPHTHALEN-2-ONE,1,1A,4,5,6,7,7A,7B-OCTAHYDRO-1,1,7,
 20  THIAZOLO\5,4-D\PYRIMIDINE,2,5-DICHLORO-
 21  PHENOL,2,6-BIS(1,1-DIMETHYLETHYL)-4-METHYL-
 22  CARBONICACID,DIPHENYLESTER
 23  ACETYLCHLORIDE,(2,4-DICHLOROPHENOXY)-
 24  PYRIDINE,3,4-BIS(P-METHOXYPHENYL)-
 25  ACETYLCHLORIDE,(2,4-DICHLOROPHENOXY)-
 26  ETHANE,1,1,2-TRICHLORO-1,2,2-TRIFLUORO-
 27  BUTANE,1,1,3,4-TETRACHLORO-1,2,2,3,4,4-HEXAFLUORO-
 28  PHENOL,2,6-BIS(1,1-DIMETHYLETHYL)-4-ETHYL-
 29  1,1'-BIPHENYL,2,2',5-TRICHLORO-
 30  BENZENE,5-(2-ISOTHIOCYANATOETHYL)-1,2,3-TRIMETHOXY-
 31  METHANONE,BIS(4-CHLOROPHENYL)-
 32  1,2-BENZENEDICARBOXYLICACID,BUTYL2-METHYLPROPYLESTER
 33  METHANONE,BIS(4-CHLOROPHENYL)-
 34  BENZENE,1,1'-(CHLOROETHENYLIDENE)BIS\4-CHLORO-
 35  METHANONE,(4-CHLOROPHENYL)(2,4-DICHLOROPHENYL)-
 36  9H-FLUOREN-9-ONE,2,7-DICHLORO-
 37  BENZENE,1,1'-(DICHLOROETHENYLIDENE)BIS\4-CHLORO-
 38  BENZENE,1,1'-(DICHLOROETHENYLIDENE)BIS\4-CHLORO-
 39  BENZENE,1,1'-SULFONYLBIS\4-CHLORO-
 40  ISOOCTANE,(ETHENYLOXY)-
 41  BENZENE,1,1'-(2,2,2-TRICHLOROETHYLIDENE)BIS\4-CHLORO-
 42  11H-DIBENZO\C,F\\1,2\DIAZEPIN-11-ONE,3,8-DICHLORO-
 43  BENZENE,1,1'-(2,2,2-TRICHLOROETHYLIDENE)BIS\4-CHLORO-
 44  1,2-BENZENEDICARBOXYLICACID,DIISOOCTYLESTER
 45  FLUORENE-9-THIOL
 46  FLUORENE-9-THIOL
 47  BENZENEMETHANOL,4-CHLORO-.ALPHA.-(4-CHLOROPHENYL)-.ALPHA.-(TRICHLORO
NO  NAME
48  1,2-PROPANEDIOL,3-(TETRADECYLOXY)-
49  2,6,10-DODECATRIEN-1-OL,3,7,11-TRIMETHYL-,(Z,E)-
50  1,2-TETRADECANEDIOL
51  BENZENE,1-CHLORO-3-(CHLOROMETHYL)-
52  4H-1-BENZOPYRAN-4-ONE,2-(3,4-DIHYDROXYPHENYL)-6,8-DI-.BETA.-D-GLUCOP

NO  M/E   SCAN    TIME   REF    RRT   METH        AREA      AMOUNT        %TOT
 1  TOT      7    0:21    3   0.101   A BB     583842.       3.429        1.49
 2  TOT     31    1:33    3   0.449   A BB    1315830.       7.727        3.35
 3  TOT     69    3:27    3   1.000   A BB   17028300.     100.000       43.41
 4  TOT    121    6:03    3   1.754   A BB      19440.       0.114        0.05
 5  TOT    132    6:36    3   1.913   A BB    2748220.      16.139        7.01
 6  TOT    135    6:45    3   1.957   A VB     612480.       3.597        1.56
 7  TOT    143    7:09    3   2.072   A BV     699392.       4.107        1.78
 8  TOT    149    7:27    3   2.159   A VB    1143930.       6.718        2.92
 9  TOT    194    9:42    3   2.812   A BB    1671050.       9.813        4.26
10  TOT    208   10:24    3   3.014   A BV      37454.       0.220        0.10
11  TOT    212   10:36    3   3.072   A VB      38514.       0.226        0.10
12  TOT    217   10:51    3   3.145   A BB     101778.       0.598        0.26
13  TOT    234   11:42    3   3.391   A VB      16280.       0.096        0.04
14  TOT    237   11:51    3   3.435   A BB      34683.       0.204        0.09
15  TOT    249   12:27    3   3.609   A BB      11972.       0.070        0.03
16  TOT    252   12:36    3   3.652   A BB      72992.       0.429        0.19
17  TOT    266   13:18    3   3.855   A BB     133946.       0.787        0.34
18  TOT    284   14:12    3   4.116   A BB     109229.       0.641        0.28
19  TOT    298   14:54    3   4.319   A BV      88496.       0.520        0.23
20  TOT    303   15:09    3   4.391   A VB     205542.       1.207        0.52
21  TOT    307   15:21    3   4.449   A VB     124208.       0.729        0.32
22  TOT    321   16:03    3   4.652   A BB      24016.       0.141        0.06
23  TOT    329   16:27    3   4.768   A BB      27187.       0.160        0.07
24  TOT    336   16:48    3   4.870   A BB       3479.       0.020        0.01
25  TOT    339   16:57    3   4.913   A BB     439992.       2.584        1.12
26  TOT    345   17:15    3   5.000   A BB       5828.       0.034        0.01
27  TOT    357   17:51    3   5.174   A BB      98896.       0.581        0.25
28  TOT    377   18:51    3   5.464   A BB      47760.       0.280        0.12
29  TOT    379   18:57    3   5.493   A BB      24011.       0.141        0.06
30  TOT    382   19:06    3   5.536   A BB      28384.       0.167        0.07
31  TOT    415   20:45    3   6.014   A BB    1916050.      11.252        4.88
32  TOT    423   21:09    3   6.130   A BV      27376.       0.161        0.07
33  TOT    429   21:27    3   6.217   A BB    2076790.      12.196        5.29
34  TOT    442   22:06    3   6.406   A BB      28992.       0.170        0.07
35  TOT    444   22:12    3   6.435   A BB      32853.       0.193        0.08
36  TOT    450   22:30    3   6.522   A BB     136019.       0.799        0.35
37  TOT    459   22:57    3   6.652   A BB    1102960.       6.477        2.81
38  TOT    473   23:39    3   6.855   A BV    3052510.      17.926        7.78
39  TOT    480   24:00    3   6.957   A VB    1544470.       9.070        3.94
40  TOT    487   24:21    3   7.058   A VB     228992.       1.345        0.58
41  TOT    494   24:42    3   7.159   A BB     350992.       2.061        0.89
42  TOT    497   24:51    3   7.203   A VB      56640.       0.333        0.14
43  TOT    508   25:24    3   7.362   A BB     499456.       2.933        1.27
44  TOT    549   27:27    3   7.957   A BB      60832.       0.357        0.16
45  TOT    553   27:39    3   8.014   A VB       8488.       0.050        0.02
46  TOT    568   28:24    3   8.232   A BB       6907.       0.041        0.02
47  TOT    594   29:42    3   8.609   A BB     195104.       1.146        0.50
48  TOT    607   30:21    3   8.797   A BB      49664.       0.292        0.13
49  TOT    612   30:36    3   8.870   A BB      48480.       0.285        0.12


NO  M/E   SCAN    TIME   REF    RRT   METH        AREA      AMOUNT        %TOT
50  TOT    626   31:18    3   9.072   A BB      20763.       0.122        0.05
51  TOT    654   32:42    3   9.478   A BB      38343.       0.225        0.10
52  TOT    682   34:06    3   9.884   A BB     244586.       1.436        0.62
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NO.	SCAN	PUR	FIT	INDEX
1	7	995	997	270
2	31	973	998	270
3	69	814	908	1191
4	121	819	829	9565
5	132	917	983	1077
6	135	906	959	5401
7	143	916	976	1077
8	149	882	919	15278
9	194	680	991	3041
10	208	562	926	1493
11	212	591	821	1079
12	217	845	963	12128
13	234	606	824	20854
14	237	738	879	12128
15	249	662	811	3683
16	252	837	968	15278
17	266	783	960	15278
18	284	408	813	10417
19	298	560	847	9200
20	303	386	799	10417
21	307	879	985	1642
22	321	397	601	936
23	329	391	758	4082
24	336	212	510	11224
25	339	419	797	4082
26	345	472	777	330
27	357	565	867	2191
28	377	628	819	7606
29	379	484	897	18298
30	382	421	773	17863
31	415	932	985	614
32	423	881	881	12130
33	429	934	986	614
34	442	596	785	4626
35	444	658	911	17110
36	450	740	978	8958
37	459	802	977	245
38	473	815	976	245
39	480	744	933	458
40	487	438	852	18318
41	494	826	971	10
42	497	580	779	4503
43	508	799	971	10
44	549	713	817	15406
45	553	297	577	12883
46	568	345	574	12883
47	594	365	744	1420
48	607	182	744	5260
49	612	737	808	7398
50	626	241	733	13495
51	654	378	842	3419
52	682	259	604	15942

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QUANTITATION REPORT         FILE: OUTLIST

DATA: 24DTANG.TI
05/11/81 16:20:00
SAMPLE: 2,4,D PROCESS WATER
 ONDS.: 50(5 MIN)-275 @ 8 DEG/MIN
 ORMULA: OV 1 COLUMN        INSTRUMENT: 4021             WEIGHT:     0.000
SUBMITTED BY: J TANG        ANALYST: JW                  ACCT. NO.:

AMOUNT=AREA * REF.AMNT/(REF.AREA* RESP.FACT)

 NO  NAME
  1  2-PENTANONE,3,3,4,4-TETRAMETHYL-
  2  ACETICACID,CHLORO-,METHYLESTER
  3  ACETICACID,DICHLORO-,METHYLESTER
  4  BENZENE,1,3-DIMETHYL-
  5  BENZENE,1,3-DIMETHYL-
  6  HEXANE,1,1'-OXYBIS-
  7  PENTANOL,2,2,4-TRIMETHYL-
  8  PHENOL,2-CHLORO-
  9  ISOOCTANOL
 10  1-HEPTANOL,6-METHYL-
 11  PHENOL,2-BROMO-
 12  ACETICACID,TRIFLUORO-,OCTYLESTER
 13  1-HEXANOL,2-ETHYL-
 14  OCTANOICACID,METHYLESTER
 15  PHENOL,2,5-DICHLORO-
 16  1-HEXENE,3,4-DIMETHYL-
 17  PHENOL,2,5-DICHLORO-
 18  PHENOL,4-CHLORO-
 19  PROPANAMIDE
 20  PHENOL,2,4-DICHLORO-6-METHYL-
 21  PHENOL,2-BROMO-4-CHLORO-
 22  BENZENE,DICHLOROMETHOXY-
 23  PHENOL,4-BROMO-
 24  BENZENE,1,3,5-TRICHLORO-2-METHOXY-
 25  1-HEPTANOL,6-METHYL-
 26  PHENOL,2,4,5-TRICHLORO-
 27  ISOOCTANOL
 28  1-HEPTYN-3-OL
 29  ACETAMIDE,N-(2,6-DICHLOROPHENYL)-
 30  CYCLOPROPANE,PENTYL-
 31  ISOOCTANOL
 32  1H-BENZOTRIAZOLE,5-CHLORO-1-(4-CHLOROPHENYL)-
 33  PHENOL,2,6-BIS(1,1-DIMETHYLETHYL)-4-METHYL-
 34  ACETICACID,SEC-OCTYLESTER
 35  2-NAPHTHALENEACETICACID,ETHYLESTER
 36  1-HEPTANOL,6-METHYL-
 37  ACETYLCHLORIDE,(2,4-DICHLOROPHENOXY)-
 38  1,3,6,9B-TETRAAZAPHENALENE-4-CARBONITRILE,7-BROMO-2-METHYL-
 39  1-HEPTANOL,6-METHYL-
 40  ACETYLCHLORIDE,(2,4-DICHLOROPHENOXY)-
 41  ACETYLCHLORIDE,(2,4-DICHLOROPHENOXY)-
 42  BUTANOICACID,4-IODO-,METHYLESTER
 43  ACETYLCHLORIDE,(2,4-DICHLOROPHENOXY)-
 44  FORMAMIDE,N-(3,4-DICHLOROPHENYL)-
 45  PHENOL,2,6-BIS(1,1-DIMETHYLETHYL)-4-ETHYL-
 46  BENZENE,1,1',1'',1'''-(1,2-ETHENEDIYLIDENE)TETRAKIS-
 47  BUTANOICACID,4-(2-METHOXY-1-METHYL-2-OXOETHOXY)-,METHYLESTER
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NO  NAME
48  ACETICACID, SEC-OCTYLESTER
49  CYCLOPENTANECARBOXYLICACID, 1-AMINO-, BIS(TRIMETHYLSILYL)DERIV.
50  ACETICACID, SEC-OCTYLESTER
51  HEPTANE, 3-\(ETHENYLOXY)METHYL\-
52  1,2-BENZISOTHIAZOLE-3-CARBOXYLICACID
53  ETHANOL, 2-(OCTYLOXY)-
54  ACETICACID, (2-CHLORO-6-METHYLPHENOXY)-
55  PENTANAL, 3-(HYDROXYMETHYL)-4,4-DIMETHYL-
56  ACETICACID, (2-CHLORO-6-METHYLPHENOXY)-
57  HEXADECANE, 1-CHLORO-
58  ETHANOL, 2-(OCTYLOXY)-
59  BUTANOICACID, 4,4'-SELENOBIS-
60  1,2,4,5-TETRAZINE, HEXAHYDRO-1,4-BIS(3-PHENYLPROPYL)-
61  .ALPHA.-D-XYLOFURANOSIDE, METHYL2-O-METHYL-
62  1,2-BENZENEDICARBOXYLICACID, DIISOOCTYLESTER
63  ETHER, BUTYLPENTYL
64  1-DODECANESULFONAMIDE, N,N-BIS(2-HYDROXYETHYL)-
65  3,7,11-TRIDECATRIENENITRILE, 4,8,12-TRIMETHYL-

NO  M/E   SCAN   TIME  REF    RRT  METH        AREA      AMOUNT       %TOT
 1  TOT     27   1:21   10  0.287  A BB      42816.       0.332       0.07
 2  TOT     29   1:27   10  0.309  A BB     544344.       4.226       0.88
 3  TOT     40   2:00   10  0.426  A BB     376192.       2.920       0.61
 4  TOT     44   2:12   10  0.468  A VV     129712.       1.007       0.21
 5  TOT     49   2:27   10  0.521  A VV     184132.       1.429       0.30
 6  TOT     52   2:36   10  0.553  A BB    1159890.       9.004       1.89
 7  TOT     67   3:21   10  0.713  A VB    2778110.      21.566       4.52
 8  TOT     76   3:48   10  0.809  A BB    1965060.      15.254       3.19
 9  TOT     81   4:03   10  0.862  A BB    8108540.      62.945      13.18
10  TOT     94   4:42   10  1.000  A VB   12881900.     100.000      20.94
11  TOT    101   5:03   10  1.074  A BB     177920.       1.381       0.29
12  TOT    110   5:30   10  1.170  A BB     598016.       4.642       0.97
13  TOT    119   5:57   10  1.266  A BV     351360.       2.728       0.57
14  TOT    125   6:15   10  1.330  A VB     166784.       1.295       0.27
15  TOT    133   6:39   10  1.415  A BB    8701360.      67.547      14.14
16  TOT    139   6:57   10  1.479  A BB     278336.       2.161       0.45
17  TOT    143   7:09   10  1.521  A BB    1795320.      13.937       2.92
18  TOT    150   7:30   10  1.596  A BB     545312.       4.233       0.89
19  TOT    153   7:39   10  1.628  A VB     227379.       1.765       0.37
20  TOT    162   8:06   10  1.723  A BB      22304.       0.173       0.04
21  TOT    165   8:15   10  1.755  A VV     252672.       1.961       0.41
22  TOT    171   8:33   10  1.819  A VB     460896.       3.578       0.75
23  TOT    177   8:51   10  1.883  A BB     259984.       2.018       0.42
24  TOT    184   9:12   10  1.957  A BB     112043.       0.870       0.18
25  TOT    189   9:27   10  2.011  A BB    1518970.      11.792       2.47
26  TOT    192   9:36   10  2.043  A VB     470291.       3.651       0.76
27  TOT    202  10:06   10  2.149  A BV    2457590.      19.078       3.99
28  TOT    208  10:24   10  2.213  A VB     456832.       3.546       0.74
29  TOT    213  10:39   10  2.266  A BB       9056.       0.070       0.01
30  TOT    219  10:57   10  2.330  A BV      94479.       0.733       0.15
31  TOT    223  11:09   10  2.372  A VV     411552.       3.195       0.67
32  TOT    230  11:30   10  2.447  A VB     401848.       3.119       0.65
33  TOT    240  12:00   10  2.553  A BB     115477.       0.896       0.19
34  TOT    248  12:24   10  2.638  A BB      97237.       0.755       0.16
35  TOT    256  12:48   10  2.723  A BV     420064.       3.261       0.68
36  TOT    259  12:57   10  2.755  A BB     877312.       6.810       1.43
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NO   M/E   SCAN    TIME   REF    RRT   METH         AREA       AMCUNT            %TDT
37   TOT    263   13: 09   10  2. 798   A BB      462848.       3. 593            0. 75
38   TOT    267   13: 21   10  2. 840   A BB      191008.       1. 483            0. 31
39   TOT    271   13: 33   10  2. 883   A BB     1633790.      12. 683            2. 66
40   TOT    274   13: 42   10  2. 915   A BV     3490390.      27. 095            5. 67
41   TOT    283   14: 09   10  3. 011   A BB       35104.       0. 273            0. 06
42   TOT    289   14: 27   10  3. 074   A BV      101080.       0. 785            0. 16
43   TOT    292   14: 36   10  3. 106   A BB      345712.       2. 684            0. 56
44   TOT    309   15: 27   10  3. 287   A BB       11152.       0. 087            0. 02
45   TOT    311   15: 33   10  3. 309   A VB       41892.       0. 325            0. 07
46   TOT    318   15: 54   10  3. 383   A BB       48640.       0. 378            0. 08
47   TOT    332   16: 36   10  3. 532   A BV       86477.       0. 671            0. 14
48   TOT    345   17: 15   10  3. 670   A BB      160576.       1. 247            0. 26
49   TOT    348   17: 24   10  3. 702   A BB       17776.       0. 138            0. 03
50   TOT    357   17: 51   10  3. 798   A BB      349952.       2. 717            0. 57
51   TOT    376   18: 48   10  4. 000   A BB       98677.       0. 766            0. 16
52   TOT    383   19: 09   10  4. 074   A BV       16395.       0. 127            0. 03
53   TOT    387   19: 21   10  4. 117   A BB      198912.       1. 544            0. 32
54   TOT    395   19: 45   10  4. 202   A BB       33456.       0. 260            0. 05
55   TOT    398   19: 54   10  4. 234   A VV      114106.       0. 886            0. 19
56   TOT    406   20: 18   10  4. 319   A BV       86720.       0. 673            0. 14
57   TOT    410   20: 30   10  4. 362   A VB      953344.       7. 401            1. 55
58   TOT    421   21: 03   10  4. 479   A BB     2764540.      21. 461            4. 49
59   TOT    426   21: 18   10  4. 532   A VB       72352.       0. 562            0. 12
60   TOT    460   23: 00   10  4. 894   A BB       15531.       0. 121            0. 03
61   TOT    470   23: 30   10  5. 000   A BB       40672.       0. 316            0. 07
62   TOT    484   24: 12   10  5. 149   A BB      312640.       2. 427            0. 51
63   TOT    523   26: 09   10  5. 564   A BB       68416.       0. 531            0. 11
64   TOT    532   26: 36   10  5. 660   A BB      237056.       1. 840            0. 39
65   TOT    540   27: 00   10  5. 745   A BB       89349.       0. 694            0. 15
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NO.	SCAN	PUR	FIT	INDEX
1	27	511	757	4233
2	29	915	960	758
3	40	935	973	1440
4	44	914	994	1165
5	49	739	946	1165
6	52	635	722	1392
7	67	635	714	5070
8	76	907	988	723
9	81	934	993	15278
10	94	906	961	5401
11	101	542	965	722
12	110	693	917	6464
13	119	781	894	1014
14	125	602	901	1302
15	133	844	987	3041
16	139	796	891	11651
17	143	880	986	3041
18	150	737	964	1079
19	153	712	803	423
20	162	569	858	5277
21	165	701	835	3900
22	171	579	936	20854
23	177	604	967	1073
24	184	841	975	539
25	189	815	969	5401
26	192	874	983	739
27	202	784	956	15278
28	208	646	758	9562
29	213	396	571	12076
30	219	460	844	6430
31	223	739	921	15278
32	230	341	621	15883
33	240	869	957	1642
34	248	466	756	20839
35	256	392	618	6714
36	259	758	861	5401
37	263	380	796	4082
38	267	223	463	18232
39	271	729	820	5401
40	274	455	806	4082
41	283	282	654	4082
42	289	366	765	10762
43	292	397	768	4082
44	309	251	736	8505
45	311	618	798	7606
46	318	356	521	3676
47	332	495	820	21450
48	345	656	849	20839
49	348	208	824	24019
50	357	701	833	20839
51	376	517	913	965
52	383	452	826	19020
53	387	427	853	9785
54	395	403	693	12723
55	398	329	795	24836
56	406	323	694	12723
57	410	434	909	8108
58	421	445	625	9785
59	426	359	625	13388
60	460	398	730	17717
61	470	405	693	16881
62	484	775	858	15406
63	523	429	754	12479
64	532	472	784	15526
65	540	689	852	8802